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Effect of uniaxial stress on luminescence of undoped and thallium-doped KI and RbI crystals

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Abstract. The effect of uniaxial stress applied at various temperatures along the ⟨100⟩ crystal axis on the self-trapped exciton (STE) and impurity-induced luminescence has been studied for pure and Tl^+, Na^+-containing KI and RbI crystals under excitation in the exciton and band-to-band absorption region as well as under x-ray excitation. An increase of the intrinsic/extrinsic emission intensity ratios has been observed and explained by the stress-induced (i) enhancement of the self-trapping efficiency of electronic excitations and the decrease of their migration length and (ii) suppression of the nonradiative decay of excitons into stable radiation defects. A strong influence of the uniaxial stress on the structure of the STE adiabatic potential energy surface has been detected in RbI which is evident in the stress-induced increase of the E_x/π and, particularly, of the σ/E_x emission intensity ratios. This effect has been connected with the increase in the energy barriers between various STE configurations in the compressed crystal lattice. The dependence of the on-centre STE emission intensity in alkali halides on the distance between the nearest lattice anions and on their size has been discussed.

1. Introduction

The relaxation of the electronic excitations in alkali halides is a process where the excited anion of the original structure of the symmetric one-halogen exciton $(\mathrm{Hal}^-)^*$ transforms into an anisotropic centre—a two-halogen exciton $(\mathrm{Hal}_2^{2-})^*$. The final structure of the relaxed crystal lattice depends on the crystal and can be a Hal_2^{2-} centre (STE) of the on-centre, weak off-centre and strong off-centre configurations [1]. In KI, two and in RbI, three of these configurations coexist. The radiative decay of each configuration is accompanied by the characteristic emission.

The intrinsic luminescence spectrum of KI consists of two bands peaking at 4.15 eV and 3.31 eV, and designated as σ and π bands, respectively [2–5]. These emissions are most effectively excited by the light from the band-to-band energy region ($E_{exc} > 6.3$ eV) as well as by x-rays. Under excitation in the first exciton absorption band the E_x emission band peaking at 3.02 eV is observed at 4.2 K.

The luminescence spectrum of RbI excited in the fundamental absorption region at low temperatures consists of three bands peaking at 3.9 eV, 3.06 eV and near 2.2 eV, and designated as σ, E_x and π bands, respectively [2, 6]. It has been found [2, 7] that, unlike KI, the E_x emission of an RbI crystal is observed upon excitation not only in the first exciton absorption band but also in the interband absorption region.

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The fast σ luminescence of both crystals arises from the singlet state and belongs to the on-centre (type I) configuration of the self-trapped exciton (STE) [1, 8]. The π bands in KI and RbI arise mainly from the triplet state and belong to the weak off-centre (type II) and strong off-centre (type III) configurations of the STE, respectively. The origin of the E_x band in KI and RbI has been discussed for a long time. A considerable number of experimental data obtained up to now point to the extrinsic origin of the E_x emission in KI (see, e.g., [9]) and to the intrinsic origin of the E_x emission in RbI [1, 8, 10–15]. In RbI, this band is ascribed to the type II (weak off-centre) STE configuration [1].

The main action of the uniaxial stress on a crystal is the compression of the crystal lattice and the lowering of its symmetry. A cubic crystal compressed along, e.g., the $\langle 100\rangle$ crystal axis becomes uniaxial and its symmetry lowers down to tetragonal. The method of the uniaxial stress has been successfully used in the spectroscopy of anisotropic defects in cubic crystals (see, e.g., [16]). Due to the anisotropy of the self-trapped electronic excitations, a considerable influence of the uniaxial stress on their relaxation process could be expected. As the size and the character of the anisotropy change in the relaxation process, the differentiation of the separate stages of this process by means of the uniaxial stress is likely to be performed. Besides the study of the influence of the uniaxial stress on the self-trapping processes and on the relaxed excited state structure of the STE, it is possible to examine the effect of the stress on the migration of the electronic excitations and anisotropic defects (H and V_K centres), appearing at the nonradiative decay of excitons, and on the efficiency of the nonradiative decay process.

The effect of the uniaxial stress supplied along the $\langle 100\rangle$ crystal axis on the luminescence of undoped alkali halides excited by x-rays and UV light has been studied in [17–19]. The main result of [17] is a strong stress-induced enhancement of both the σ and π emission bands in the x-ray excited luminescence spectrum of KCl, KBr and KI crystals. The effect is the smallest in KCl, it is larger in KBr and the largest in KI where the emission intensity increases more than tenfold. The stress-induced redistribution of the E_x and π emission intensities has also been observed in the RbI crystal [18]. The enhancement of the π emission and the reduction of some nonidentified impurity emissions have been detected in CsI crystal, uniaxially stressed at 80 K [19]. It has been suggested that this effect is caused by the stress-induced increase of the exciton self-trapping efficiency and the decrease of its migration length. To check this suggestion, it was necessary to expand the investigations of the uniaxial stress effect on some other, e.g., doped crystals, and to study in more detail the stress-induced changes in the efficiency of energy transfer to impurities and some other crystal structure defects.

The aim of the present paper is to obtain some additional information about the influence of the uniaxial stress on the intrinsic and extrinsic luminescence and to establish the causes of the intrinsic luminescence enhancement in the uniaxially stressed crystals on the basis of the obtained results. The stress-induced changes in the intensities of various intrinsic luminescence bands (σ, π and E_x) as well as in the efficiency of the radiation defect creation have also been studied. For the first time, the effect of the uniaxial stress on the migration and self-trapping of electronic excitations has been studied under the stress supplied at 4.2 K.

To perform these investigations, pure and thallium-doped KI and RbI crystals have been chosen for the following reasons: (i) according to [17], in KI the stress-induced enhancement of the intrinsic luminescence is the largest; (ii) the exciton migration length in KI and RbI is large at 4.2 K and considerable also at 80 K [20], which allows us to hope for noticeable stress-induced effects; (iii) the emission of Tl^+ centres, due to its large intensity, small halfwidth of the emission bands and their weak overlapping with the exciton emission bands, is suitable for the study of the electronic excitation migration; moreover, the Tl^+ concentration in the crystal can be easily varied and determined from the optical absorption spectra.

2. Experimental procedure

Single crystals of undoped KI and RbI as well as KI:Tl and RbI:Tl crystals were grown in Tartu by the Stockbarger method in vacuum from the zone-refined salts. The concentration of TlI in the melt in KI:Tl varied from 3×10^{-4} to 2 mol% while in RbI:Tl it was 2×10^{-2} mol%. For KI:Tl, the actual concentration of Tl^+ ions in the samples studied was determined from the absorption spectrum of Tl^+ centres. The samples with dimensions of about $5 \times 5 \times 3$ mm^3 were cut out along the $\langle 100 \rangle$ crystal axes, ground and polished to have two plane parallel surfaces. Spectral measurements were carried out by means of two different experimental set-ups. For the measurements at 80 K under both the x-ray and UV excitation a special nitrogen cryostat was used. The uniaxial compression of the crystal was produced by the stop screw turn and measured in the values of $\Delta l/l$ (%), where l stands for the sample length along the stress axes. The compression includes both the elastic and the plastic deformation. At the removal of the stress the first one disappears, while the second one remains. The stress-induced effects obtained in this work are reversible and, hence, connected with the elastic part of the crystal compression. A crystal was excited by x-rays (120 kV, 4 mA) or by the deuterium lamp light through a vacuum monochromator VMR-2. The emission spectra were detected through an MDR-2 monochromator using a cooled FEU-106 photomultiplier operating in the photon counting mode.

The experiments at 4.2–80 K under excitation in the exciton absorption region were carried out by means of the set-up described in [21]. The luminescence was excited with the light of the deuterium DDS-400 lamp through the quartz prism monochromator SF-4. A specially designed helium cryostat described in detail in [22] was used. It enables us to apply the variable compressive uniaxial stress and to perform the optical measurements at any temperature from 1.7 to 300 K. The stress was applied at various temperatures along the [001] crystal axis, perpendicular to the directions of both the excitation and the observation of the luminescence. The angle between the crystal front plane and these directions was near to 45°.

All spectra were corrected for the spectral distribution of the excitation energy, transmission and dispersion of the monochromators and the spectral sensitivity of the photomultiplier.

3. Experimental results

We have found that the stress-induced effects observed in the crystals studied depend strongly on the luminescence excitation energy, temperature at which the uniaxial stress is supplied and the concentration of thallium in the crystal. The stress supplied at 4.2 K results in the decrease of the intensities of all the emission bands excited in the exciton absorption region. For all alkali halides this decrease probably stems from the same reasons which have been discussed in [22]. Therefore, in this case it is only the intensity ratios of the investigated emission bands that can be compared and discussed. The effect of the uniaxial stress supplied at 4.2 K on the emission intensity ratios is relatively small. If the stress is supplied at higher temperatures followed by cooling of the stressed crystal down to 4.2 K, the effect is remarkably larger.

The influence of the uniaxial stress on the optical characteristics of the crystals studied appears in the four following effects: (i) in the redistribution of the intensities of the intrinsic and extrinsic emission bands; (ii) in the reduction of the efficiency of radiation defect creation by x-rays at 80 K; (iii) in the redistribution of the intensities of the STE emission bands; (iv) in the appearance of new luminescent defects under strong stress. The effect (i) is more evident in undoped and doped KI crystals whereas the effect (iii) in RbI crystals; the effects (ii) and

(iv) are detected in both the KI and RbI crystals. In the present paper, we consider the first three effects. Some preliminary results of their study have been briefly reported in [23]. The effect (iv) has been examined in [24].

3.1. Uniaxial stress effect on the intensity of the intrinsic and extrinsic emission bands

The x-ray excited luminescence spectra measured at 80 K for the unstressed and for the uniaxially stressed at 80 K KI:Tl crystals with various Tl^+ concentrations are shown in figure 1. One can see that as the stress grows, the intensity of the intrinsic σ and π emission bands increases in all the samples studied. The value of the increase is the largest in the KI crystals with the smallest Tl^+ content (figure 1(a)) and it decreases as the impurity concentration increases (figures 1(b) and 1(c)). An analogous effect is observed in KI containing Na^+ ions. In KI with a small Tl^+ concentration (figure 1(a)), besides a drastic enhancement of the σ and π emissions, the increase of some lower-energy emissions (curve $3'''$), strongly overlapping with the weak 2.85 eV emission of Tl^+ centres, is observed (see the decomposition of spectrum 3 in figure 1(a) into single components). As these emissions are effectively produced by the x-ray excitation and are weak under the UV excitation (figure 2(a)), one may assume that they accompany the recombinations of radiation defects. The creation efficiency of these defects (V_K, V_{KA}, F′, F centres) under the x-irradiation of the stressed crystals may be large [17]. For example, that may be the emission appearing as a result of tunnelling transitions between the ground states of adjacent F′ and V_K centres [25]. The uniaxial stress-induced enhancement of the recombination luminescence has been observed in [17] for KCl and KBr crystals and explained by the increase of the tunnelling recombination probability due to the orientation of the defects under the stress. Owing to the growth of these emissions under the stress, it is difficult to define the changes in the intensity of the Tl^+ emission. However, for KI:Tl (3×10^{-2} mol% of Tl^+) it is clearly seen that the increase of the σ and π bands is accompanied by a corresponding reduction of the Tl^+-induced emission intensity (figure 1(b)). In KI:Tl containing about 1 mol% of Tl^+ in the crystal the intensities of the σ and π bands also increase, but the intensity of Tl^+ emission becomes saturated (figure 1(c)). The effect of the uniaxial stress supplied at 80 K on the luminescence of KI:Tl crystals with various Tl^+ concentrations has been investigated also under excitation by the UV light with the energy corresponding to the creation in the crystal of the electron–hole pairs (7.7 eV) or excitons (6.0 eV) (see figures 2(a), (c), (e) and (b), (d), (f), respectively). Like in the previous case, the stress-induced increase of the σ and π emission intensity has been registered under this excitation. However, the effect observed in this case is smaller than that observed under the x-ray excitation, and it decreases as the excitation energy becomes lower and/or the concentration of Tl^+ increases. After the emission spectrum of KI:Tl (3×10^{-2} mol%) has been decomposed into single components (see figure 2(c)), the stress-induced increase of the σ and π bands and the decrease of Tl^+ emission becomes visible. The dependence of the observed effect on the excitation energy can be explained by a great difference in the excitation penetration length into a crystal in case of the x-ray excitation and the UV excitation. As it is evident from figure 2, under the UV excitation whose penetration length, as compared with the x-ray excitation, is small, the intrinsic emission bands are intense even in a specially unstressed sample. One can assume that it is caused by the strong distortion of the near-surface layer which stimulates exciton self-trapping in this region. For that reason the effect of the external uniaxial stress under the UV excitation is small. Unlike this case, the x-ray excitation penetrates deeply into the crystal where the distortion of the crystal lattice is much smaller and, as a result, the intrinsic emission in unstressed samples is weak (figure 1). The difference in the stress-induced effects observed under the x-ray and UV excitations may also be caused by the fact that the energy of the created electronic excitations is larger in the case of the x-ray excitation than in case of the UV excitation used in the present paper. Due to these factors the effect of the external uniaxial stress under the x-ray excitation is noticeably larger than under the UV excitation.

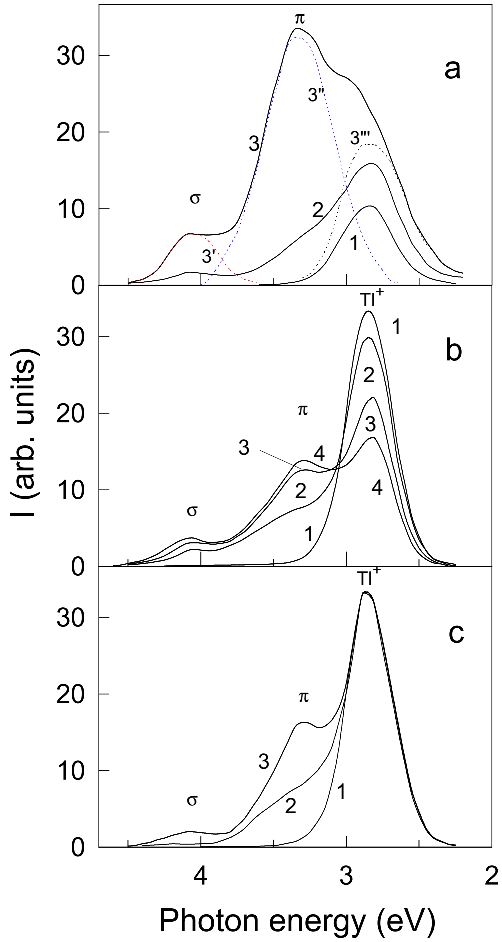

Figure 1. Emission spectra of KI:Tl crystals containing (a) 1×10^{-4}, (b) 3×10^{-2} and (c) 1 mol% of Tl^+ ions measured at 80 K under x-ray excitation without a stress (curves 1) and under the uniaxial stress supplied at 80 K (curves 2, 3, 4). (a) $p = 0.5\%$ (curve 2) and 4% (curve 3); (b) $p = 2\%$ (curve 2), 3% (curve 3) and 4% (curve 4); (c) $p = 2\%$ (curve 2) and 4% (curve 3). Spectrum 3 is decomposed into the σ (curve 3′), π (curve 3″) and remaining (curve 3‴) bands.

In figure 3, the emission spectra of the unstressed RbI:Tl crystal (curve 1) and of the same crystal uniaxially stressed at 295 K (curve 2), measured at 4.2 K under the 6.15/5.7 eV excitation, are shown. It is seen that the ratios of the intensities of the intrinsic σ, E_x and π emission bands to the intensities of the extrinsic emission bands, the A_T and A_X bands of Tl^+ centres (3.4 eV and 2.85 eV, respectively) and Na^+-induced 2.55 eV band, increase (the compared emission regions are indicated by arrows). Some dependences of the emission intensity ratios on the stress supplied at 4.2 K (a) and at 80 K (b) are shown in figure 4 for RbI (a) and RbI:Tl (b). It is evident that the extrinsic/intrinsic emission intensity ratios decrease as the stress grows (curves 1 and 2). The same effect appears in the excitation spectrum measured

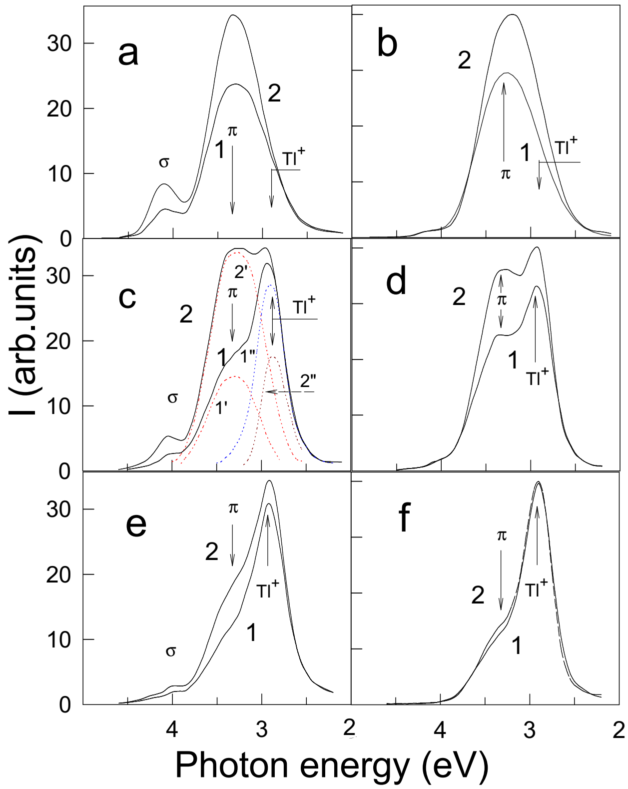

Figure 2. Emission spectra of KI:Tl crystals containing (a), (b) 1×10^{-4}, (c), (d) 3×10^{-2} and (e), (f) 1 mol% of Tl^+ ions measured at 80 K under 7.7 eV (a), (c), (e) and 6.0 eV (b), (d), (f) excitation without a stress (curves 1) and under the uniaxial stress $p = 2\%$ supplied at 80 K (curves 2). Spectra 1 and 2 in figure 2(c) are decomposed into the π (curves 1′ and 2′) and Tl^+ (curves 1″ and 2″) bands.

for the emission of Tl^+ centres in RbI:Tl (figure 5). Under excitation of the A_X emission in the Tl^+-induced absorption bands (e.g., at 5.35 eV, indicated by the arrow) its intensity is almost independent on the stress, while under excitation in the exciton absorption region (e.g., at 5.9 eV, indicated by arrow) it decreases noticeably as the stress increases (compare curves 1 and 2). Due to that the 5.35 eV/5.9 eV intensity ratio increases (curve 3).

Thus, for the example of KI:Tl and RbI:Tl crystals it is shown that under uniaxial stress the intrinsic/extrinsic emission intensity ratio considerably increases. In KI:Tl, under any type of excitation the stress-induced increase is observed for both the σ/Tl^+ and the π/Tl^+ emission intensity ratios. In RbI:Tl, the stress-induced increase of the σ/Tl^+ ratio is also considerable (particularly under the x-ray excitation) but the E_x/Tl^+ and especially π/Tl^+ emission intensity ratios change less.

As mentioned above, the effect of the stress supplied at 4.2 K is small. At $T < 30$ K the temperature dependences of the emission intensities of the intrinsic σ and π bands (figure 6(a)) and of the A_X emission of Tl^+ centres (figure 6(b)) measured for the stressed (curves 1′, 2′, 3′) and the unstressed (curves 1, 2, 3) sample under excitation in the exciton absorption band almost coincide. However, with a further rise in temperature the STE emission intensity increases and the Tl^+ emission intensity decreases more noticeably in the stressed sample than

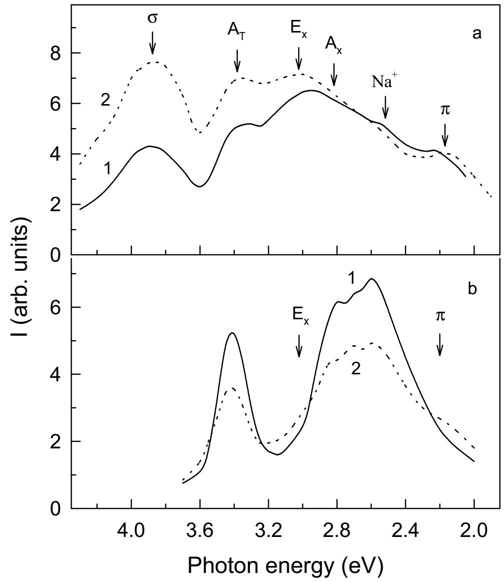

Figure 3. Emission spectra of RbI:Tl measured at 4.2 K under the 6.15 eV (a) and 5.7 eV (b) excitation for $p = 0$ (curve 1) and $p = 0.435$ kg mm^{-2} supplied at 295 K (curve 2).

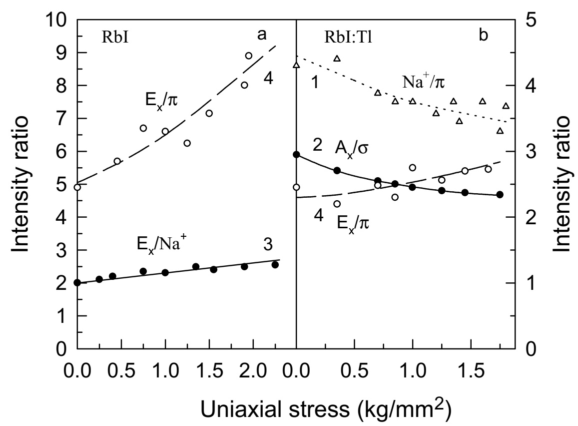

Figure 4. Dependences of the emission intensity ratios on the stress supplied (a) at 4.2 K for RbI and (b) at 80 K for RbI:Tl measured under the 6.15 eV excitation at (a) 4.2 K and (b) 80 K for the Na^+/π (curve 1), A_X/σ (curve 2), E_x/Na^+ (curve 3) and E_x/π (curves 4) intensity ratios. The data are taken from the uncorrected emission spectra measured at each value of p.

in the unstressed one. Thus, the effect of the uniaxial stress is temperature dependent and appears more clearly at higher temperatures.

3.2. Effect of uniaxial stress on the efficiency of the radiation defect creation

Recently, the effect of the uniaxial stress on the efficiency of stable radiation defect creation has been studied for a KI crystal [23, 26]. It has been found that in the stressed sample the number of the radiation defects created by x-rays at 80 K is smaller by about an order of magnitude

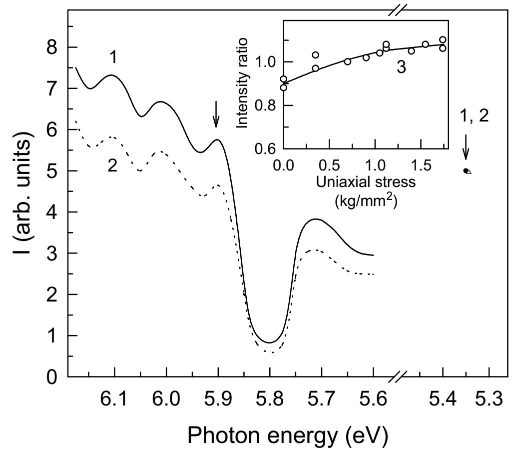

Figure 5. Excitation spectra measured at 4.2 K for the A_X emission of Tl^+ centres in RbI:Tl at $p = 0$ (curve 1) and $p = 0.87$ kg mm^{-2} supplied at 295 K (curve 2). The intensities at $E_{exc} = 5.35$ eV (the C band of Tl^+) are normalized (see two points under the arrow). Dependence of the 5.35 eV/5.9 eV intensity ratio on the stress (curve 3).

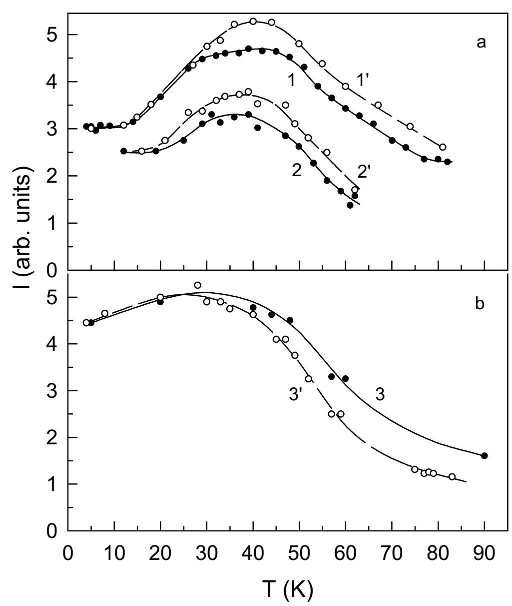

Figure 6. Temperature dependences of the intensities (normalized at 4.2 K) measured for the RbI:Tl crystal at the 3.9 eV (curves 1, 1′), 2.1 eV (curves 2, 2′) and 2.8 eV (curves 3, 3′) emission energies of RbI:Tl without stress (curves 1, 2, 3) and under the uniaxial stress (a) $p = 0.705$ kg mm^{-2} and (b) $p = 0.365$ kg mm^{-2} (curves 1′, 2′, 3′) supplied at 4.2 K. $E_{exc} = 6.15$ eV.

than that in the unstressed crystal. It is difficult to explain such a drastic decrease in the defect creation efficiency by some changes in the secondary processes (e.g., by the recombination or association of defects). Probably, this effect is caused by the stress-induced decrease in the creation efficiency of the primary radiation defects (F, H pairs).

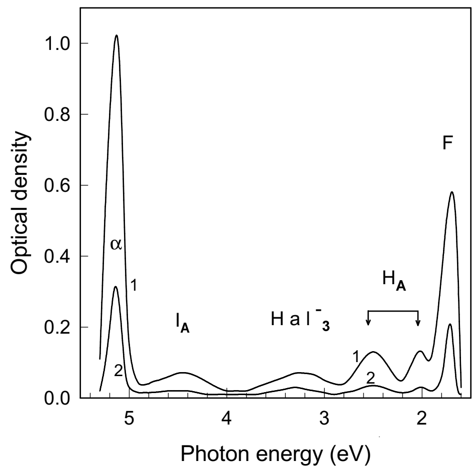

Figure 7. Absorption spectra of the RbI crystal x-irradiated at 80 K measured at 80 K for an unstressed sample (curve 1) and for the sample uniaxially stressed by ∼2% at 80 K (curve 2).

In the present paper, similar results have been obtained for an RbI crystal. The absorption spectra of unstressed (curve 1) and stressed up to 2% (curve 2) crystals x-irradiated at 80 K are compared in figure 7. The main radiation defects created by the x-irradiation at 80 K are F centres and complementary centres with the structure of the Hal_3^- molecular ion. I_3^- centres in RbI (so-called V_4 centres) appear as a result of the interaction of the two primary H centres [27]. As each RbI sample used contains a noncontrolled amount of Na^+, the impurity interstitial radiation defects (H_A and I_A centres [28]) and anion vacancies (α centres) are also produced by x-rays. From figure 7 one can see that the efficiency of the creation at 80 K of the stable radiation defects in stressed RbI is several times smaller than that in an unstressed crystal.

3.3. The effect of the uniaxial stress on the STE luminescence spectrum

As seen from figure 8, the contribution of the σ band to the luminescence spectrum, measured under excitation in the exciton absorption region for the RbI crystal stressed at 295 K, is larger than in the spectrum of the unstressed sample (compare curves 1 and 1′). As a result, the π/σ and E_x/σ emission intensity ratios decrease as the stress increases (see, e.g., curve 2). The predominant increase of the σ band with respect to the other STE emission bands is found also in the RbI:Tl crystal stressed at 295 K (figure 3). The stress-induced increase is observed for the E_x/σ emission intensity ratio as well (figure 8, curve 3). This effect is detected for RbI and RbI:Tl crystals under the stress supplied also at 4.2 K and 80 K, respectively (figures 4(a) and 4(b), curves 4) (see also [18]).

Similarly to the case of KI:Tl, the effect of the uniaxial stress is the highest for x-ray excitation and at the temperatures where the crystal is plastic. In the x-ray-excited luminescence spectrum of the unstressed RbI:Tl crystal the weak σ and π bands of the STE and the stronger impurity-induced bands peaking at 2.85 eV and 2.55 eV are observed at 80 K (figure 9, curve 1). The 2.85 eV band belongs to Tl^+ centres and the 2.55 eV band must be connected with the presence of Na^+ ions in the samples studied. The E_x emission is very weak at 80 K. The supply of uniaxial stress at 80 K brings about a drastic increase in the x-ray excited intrinsic luminescence of RbI:Tl (curve 2). The effect is particularly high for the σ emission

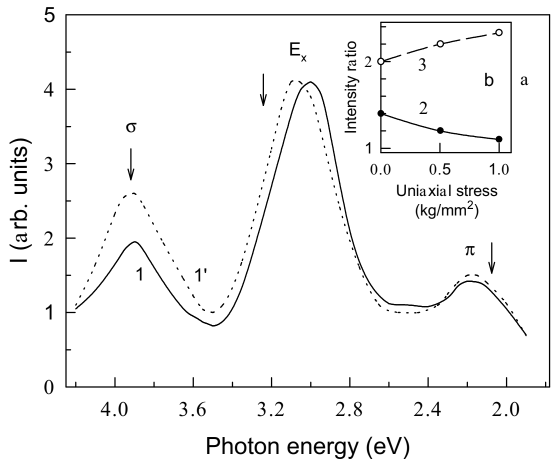

Figure 8. Normalized emission spectra of RbI measured at 4.2 K under the 6.15 eV excitation for $p = 0$ (curve 1) and $p = 1$ kg mm^{-2} supplied at 295 K (curve 1′). Dependences of the E_x/σ (curve 2) and E_x/π (curve 3) emission intensity ratios on the uniaxial stress taken at the emission energies indicated by arrows. The higher-energy shift of the ∼2.9 eV band is due to the increase of the E_x emission intensity with respect to that of some extrinsic emissions.

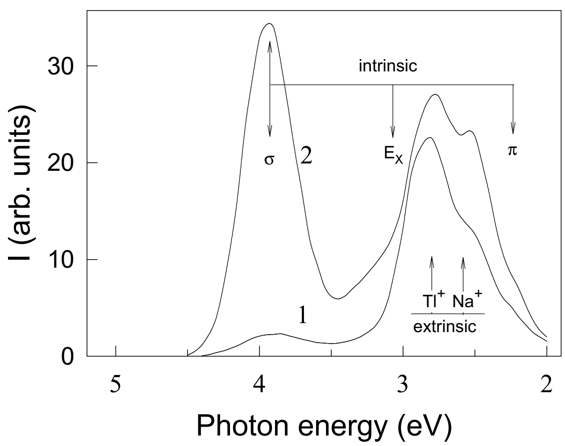

Figure 9. Emission spectra of RbI:Tl measured at 80 K under the x-ray excitation for the unstressed sample (curve 1) and for the sample uniaxially stressed at 80 K by about 2% (curve 2).

where a 16-fold increase is observed. At the same time the π emission intensity increases no more than 1.5 times. As a result, the σ/π emission intensity ratio increases essentially and so does the σ/Tl^+ emission intensity ratio. As in the case of KI:Tl, in RbI:Tl stress-induced enhancement of the recombination luminescence (connected, most probably, with the $\{V_{KA}$–$F'\}$ recombinations whose efficiency increases due to the orientation of the anisotropic radiation defects by the uniaxial stress) is observed in the 2.7–2.3 eV spectral range.

Thus, under uniaxial stress the drastic redistribution between various (σ, E_x, π) intrinsic emission bands is observed in the luminescence spectrum of an RbI crystal. However, unlike in the case of RbI, no stress-induced change has been detected in the σ/π emission intensity ratio of a KI crystal. This conclusion is confirmed by the decomposition into single components of the emission spectra shown in figure 2(c): almost the same (about twofold) stress-induced increase of both the σ and π bands is observed in the KI:Tl (3×10^{-2} mol%) crystal (compare curves 1 and 2). The differences in the σ/π ratio observed for KI:Tl crystals with different Tl^+ concentrations can be explained by the reabsorption of the σ emission in the A absorption band (4.3 eV) of Tl^+ centres which increases as the Tl^+ concentration grows.

4. Discussion

The results obtained in the present paper for undoped and thallium-doped KI and RbI crystals have allowed us to conclude that under the uniaxial stress supplied at any temperature the intrinsic/extrinsic emission intensity ratios increase. In [19], the analogous conclusion has been made for a CsI crystal and the hypothesis proposed for an explanation of this effect. It has been suggested that due to the stress-induced lowering of the crystal lattice symmetry, the free exciton migration length decreases and its self-trapping probability increases. This results in decrease of the energy transfer efficiency and in the increase of the STE luminescence intensity. Due to that the excitons cannot reach impurity ions or other lattice defects or imperfections, and the intensity of the extrinsic emission bands decreases.

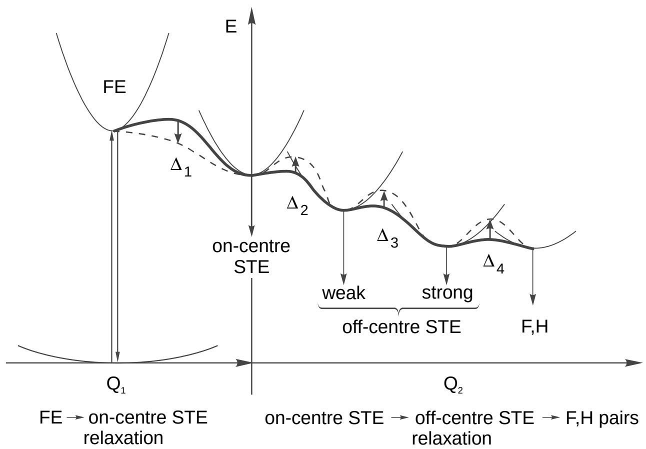

Figure 10. Schematic configuration coordinate diagram for states of the FE–STE–F, H system without stress (solid line) and under uniaxial stress (dotted line). The left side of the figure is made on the basis of the data of [29, 30] and the right side, on the basis of [13]. The coordinate Q_1 includes the shifts of the adjacent halogen ions to each other along the $\langle 110 \rangle$ axis in the process of the Hal_2^- molecular ion formation. The coordinate Q_2 includes the shift of the Hal_2^- molecular ion towards the interstitial position.

The stress-induced redistribution of the intensities of the intrinsic and extrinsic emission bands depends on Tl^+ concentration in the KI crystal (see figures 1 and 2). Let us consider this dependence for the case of exciton creation by UV light (figures 2(b), 2(d), 2(f)) when the exciton migration length in unstressed KI at 80 K is several hundred lattice constants [20]. It is essentially larger than the average distance between Tl^+ ions in all the KI crystals investigated in the present paper, and is responsible for the high efficiency of Tl^+ excitation (see figures 2(b) and 2(d)). The stress-induced effects become weaker as the impurity concentration grows, and disappear if the exciton migration length in the stressed crystal is equal to the distance between Tl^+ ions. From figure 2(f) one can see that it occurs only in KI with a large Tl^+ concentration where the distance between Tl^+ ions is several lattice constants. This consideration enables us to estimate that under stress the free exciton migration length may decrease more than an order of magnitude.

It is known [20, 29, 30] that in alkali halides the states of the free exciton and the self-trapped exciton (FE and STE) coexist and are divided by the potential energy barrier. The efficiency of the exciton energy transfer to impurities or crystal lattice imperfections at low temperatures (at least at $T < 100$ K) is conditioned by the efficiency of the resonance migration of the free excitons. One may suggest that the uniaxial stress results in a noticeable decrease of the potential barrier for the exciton self-trapping (Δ_1) (see the left side of figure 10). The stress-induced decrease of the barrier is likely to occur also in case of the self-trapping of holes, since the effect has been observed at electron–hole pair creation by UV light as well (figure 2). Under the x-ray excitation (figure 1), both the excitons and electron–hole pairs are produced, thus, the final effect of the stress may be the summary one.

Let us note that hydrostatic pressure induces the opposite effects in KI and CsI crystals [31, 32]: the pressure stabilizes the free exciton (and free hole) states and enhances the potential barrier for their self-trapping. It leads to an increase of the lifetime and migration length of the free excitons and holes. The hydrostatic pressure reduces the lattice constant but does not affect the crystal lattice symmetry, while the uniaxial stress reduces both the distance between the ions (along the compression axis) and the symmetry; as a result, the crystal becomes anisotropic. It has been shown theoretically [33–35] that if exciton motion is distorted at least in one direction, the FE states are unstable and the excitons are always self-trapped. Our results may be considered as an experimental confirmation of such a point of view.

However, the stress-induced increase of the self-trapping efficiency alone cannot be responsible for all the effects observed, as the largest stress-induced enhancement of the intrinsic emission bands is detected just in undoped or slightly doped samples and it is not completely compensated by the reduction of the extrinsic bands. There has to be another source for the intrinsic luminescence intensity growth. As is well known (see, e.g., the monographs [13, 29]), the decay of the STE can be not only radiative but also nonradiative. The latter is accompanied by radiation defect creation. The results of the present paper as well as [23, 26] show that under uniaxial stress the number of the radiation defects created at 80 K in KI and RbI by x-rays decreases several times. A hypothesis may be proposed that the stress-induced closure of the nonradiative channel of excitons decay, and, consequently, the increase of their radiative decay efficiency may be another reason for the intrinsic luminescence enhancement in the stressed KI and RbI crystals.

Another interesting result concerning the uniaxial stress effect on the relaxation processes of the radiatively decaying STE is the stress-induced redistribution of the intensities between various intrinsic emission bands. This effect is observed in RbI but it is absent in KI. The drastic stress-induced enhancement of the σ emission in RbI and RbI:Tl manifests that the on-centre configuration of the STE is a more likely configuration where an exciton relaxes in the uniaxially stressed crystal. Besides the increase in the σ/π and the σ/E_x intensity ratio, the increase in the E_x/π ratio is also observed. These data point to the fact that under the uniaxial stress the relaxation of the exciton occurs rather into the weak off-centre configuration than into the strong off-centre configuration. The increase of the E_x/π ratio in RbI has been detected not only under the uniaxial stress but also as a result of the introduction of smaller anions (e.g., Br^- ions) [36] or cations (e.g., Cs^+ ions) [37] into the RbI crystal lattice as well as under hydrostatic pressure [38].

As can be seen from figure 10, the STE is first created in the on-centre configuration. Then, by relaxation along the Q_2 coordinate, the Hal_2^- ion is gradually shifting to the interstitial position along the ⟨110⟩ direction. As a result, the weak off-centre and strong off-centre STE configurations and, finally F, H pairs may be created. This 'off-centre instability' conception appears on the basis of the numerous investigations refereed in the monographs [13, 29] as well as in the recent works carried out by means of the femtosecond spectroscopy methods [38]. All the three types of STE emission, the on-centre, weak off-centre and strong off-centre STE luminescence (σ, E_x, π), are observed in RbI, but in KI only on-centre and weak off-centre STE emissions (σ and π) have been registered. This difference is connected with the height of the barriers between different STE configurations: in KI the barriers (particularly Δ_3) are larger than in RbI where the STE minima are located on a very flat potential energy surface, i.e. Δ_3 is very small (~1 meV) [12, 36].

Both the stress-induced decrease of F, H pair creation efficiency and the increase of the σ/π and E_x/π emission intensity ratios indicate that the stress enlarges the barriers Δ_2, Δ_3 and possibly Δ_4 (figure 10).

The effect induced in RbI by the hydrostatic pressure is similar: the increase of the E_x/π ratio has been observed already at small compressions [38, 39]. The σ/E_x ratio also increases, but under a very high (0.6 GPa) hydrostatic pressure [39].

In our opinion, all these effects are caused by the compression of the RbI crystal lattice. Indeed, the uniaxial stress supplied along the ⟨100⟩ crystal axis leads to the expansion of the crystal in two ⟨110⟩ directions on the plane perpendicular to the axis of the stress and to its compression in the rest of the four ⟨110⟩ directions, so the value of the lattice compression is in an order of magnitude larger than the value of its expansion. The relaxation of the exciton occurs rather in the direction of the compression as in this direction two anions are closer to each other and due to that the formation of the two-halogen exciton needs less energy.

The effect of the crystal lattice compression may be considered as the decrease of the Rabin–Klick parameter S/D [1] (S is the space between the two adjacent halogen ions along the ⟨110⟩ direction and D is the diameter of the halogen atom). The decrease of the distance S between the two halogens results in the increase of the repulsion forces between them. It leads to the growth of the potential barriers between various minima. As the on-centre minima of the STE are initially populated, the smaller is the S/D ratio, the larger is the potential barrier between the on-centre and off-centre configurations. Due to that the σ luminescence arising from the on-centre minima must be relatively more intense. In [18], a drastic change has been observed in the decay kinetics of the E_x and π emission of RbI under the uniaxial stress supplied at 4.2 K, pointing to the decrease of the probability of the nonradiative transitions from the E_x state. This effect clearly indicates that the stress-induced increase of the potential barrier occurs also between the E_x and π minima.

In a KI crystal the S/D ratio is about 0.36 [1], i.e. it is considerably smaller than in an RbI crystal (0.42). It means that the energy barrier Δ_2 between the minima corresponding to the on-centre and off-centre STE configurations may be considerably larger in KI than in RbI. For that reason uniaxial stress supplied to the KI crystal cannot exert any noticeable influence on the height of the barriers and, consequently, the depths of the corresponding minima. It explains the absence of the stress-induced redistribution of the intensities of the intrinsic emissions in KI.

It is known (see, e.g., the monographs [13, 29]) that the efficiency of the radiation defect (F, H pair) creation at 4.2 K in KI is very low. The luminescence from the strong off-centre configuration is also absent. It means that the barriers Δ_3 (and probably Δ_4 at 4.2 K) are very high. The gradual increase of the efficiency of F, H pair creation is observed with the growth of temperature from ~40–50 to 200 K. At 80 K the coloration efficiency is already noticeable. In our opinion, the increase of the colourability is connected with a gradual expansion of the lattice during the crystal heating (the lattice constant increases in KI by about 0.4–0.5%

under crystal heating from 40 to 200 K). As it has been shown in [23, 26], the uniaxial stress supresses the efficiency of the radiation defect creation in KI at 80 K by more than an order of magnitude. These effects can be explained by the change in the S/D ratio: the increase of S/D at thermal expansion of the crystal leads to the decrease of Δ_3 and Δ_4, while the uniaxial stress-induced decrease of S/D results in the growth of Δ_3 and Δ_4. In other words, the uniaxial stress-induced lattice compression (the elastic part of that is about 0.1–0.5%) is comparable with that occurring at the cooling of the crystal. Of course, besides the F, H pair creation through the 'off-centre instability' (where the on-centre STE is converted into the strong off-centre STE which may be considered as a close F, H pair [40]), the defects may be created through the 'dynamical instability' [38], where the F, H pairs and the on-centre STE are formed from the same highly excited states, i.e. at the initial stages of the electronic excitation relaxation. This process is especially vital for the relaxation of the electron–hole pairs. The uniaxial stress may affect this mechanism, too. However, further investigations are necessary for the discussion of this influence.

The decrease of the efficiency of the radiation defect creation has been detected also under strong (0.8 GPa) hydrostatic pressure [41]: the number of F centres decreases in NaCl and KBr at 80 K and especially in KBr, at 10 K. In the uniaxially stressed KBr the efficiency of the radiation defect creation at 80 K does not change [26] which is obviously connected with the stronger compression of the crystal by the hydrostatic pressure.

Thus, if the increase of the self-trapping probability in the uniaxially stressed KI and RbI crystals is conditioned by the lowering of the translation symmetry, the further relaxation of the STE is determined by lattice compression in the closest vicinity of the relaxing STE. The first effect is opposite to that caused by the hydrostatic pressure, but the second one is the same and leads to the increase of the energy barriers on the way of the STE off-centre relaxation.

This paper reveals that the structure of the STE states in RbI is very sensitive to crystal lattice distortion. The depth of the minima of various STE configurations and the energy barriers between them are likely to change. The choice of crystals with extremely small S/D ratios (i.e. with the largest anions and the smallest cations) or the compression of the crystal lattice will result in the appearance or enhancement of the on-centre STE luminescence which, owing to its fast decay time, is very important for scintillators. We expect that the study of the spectra, decay kinetics and polarization of the STE luminescence and the temperature dependences of these characteristics under the uniaxial stress supplied along various crystal directions will give a lot of new information about the detailed structure of the STE states in alkali halides. It should also be of special interest to study in more detail the effect of the uniaxial stress on the radiationless processes occurring in these systems (see, e.g., [42]). These investigations are under way.

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