Features of the action of an uniaxial deformation on the radiative annihilation of excitons in KBr crystal

K Shunkeyev, N Zhanturina, Z Aimaganbetova, L Myasnikova, A Barmina, Sh Sagimbaeva and D Sergeyev
Zhubanov Aktobe Regional State University, 34 A. Moldagulova Ave., Aktobe, 030000, Kazakhstan

E-mail: nzhantrina@mail.ru

Abstract. To study the effect of uniaxial deformation by <100> and <110> directions on the radiative annihilation of self-trapped excitons (STE), the experiments were carried out with KI, KCl and KBr crystals. At deformation by <110> direction, the band with a maximum at 2.95 eV with a large relative Stokes shift ($S_R = 0.56$) in KBr crystal, characteristic for STE with a strongly asymmetric configuration, was detected. In crystals KI and KCl at deformation by <110> direction and in KBr crystal by <100> direction, no additional bands were detected besides intrinsic $\sigma$, $\pi$ luminescence. The appearance of an exciton with a strongly asymmetric configuration in KBr crystal is explained on the basis of the ratio of the radii of the anion and the cation, and also on the basis of the energy of excitons with different configurations on the surface of the adiabatic potential for the KI, KBr, and KCl crystals. For KBr crystal the ratio is 1.9, which is greater than in KI. The energy of the configuration transformations in KBr crystal is the smallest.

1. Introduction
The decrease in the symmetry of the lattice of alkali halide crystals by plastic and elastic deformation leads to an increase in intrinsic luminescence, as the radiative relaxation of self-trapped excitons (STE) at regular lattice sites.

Very promising are the studies of the radiative relaxation of STE at different deformation directions, since their structure has an orientation <110> in KI, KCl, and KBr crystals. To study the effect of uniaxial deformation by <100> and <110> directions on the radiative annihilation of STE, the experiments were carried out with KI, KCl and KBr crystals.

The peculiarities of such influence are determined by different configurations of STE in alkali halide crystals [1]. The basis for the classification of STE are the values of the relative Stokes losses of luminescence $S_R = \frac{E_{\chi} - E_{\sigma,\pi}}{E_{\chi}}$, where $E_{\chi}$ is the positions of the maxima of absorption bands of free excitons with $n=1$; $E_{\sigma}$ and $E_{\pi}$ are the positions of the luminescence maximums of singlet ($\sigma$) and triplet ($\pi$) STE, respectively.

Uniaxial elastic low temperature directional deformation by <100> promotes the formation of a more symmetrical configuration STE in the direction strong $\rightarrow$ weak $\rightarrow$ on in crystals KI, KCl and KBr [2].
2. Experimental results and discussion

The experimental results of X-ray luminescence (XRL) spectra for low temperature uniaxial (<110>) deformations of KBr crystal by <100> and <110> directions are presented in figures 1 and 2.

![Figure 1](image1.png)
![Figure 2](image2.png)

Figure 1. The spectra of X-ray luminescence of KBr crystal at 100K before and at low-temperature deformation (ε=1.5%) by crystallographic direction <100>. 1 – before deformation; 2 – at uniaxial deformation (100 K); 3 – after removal of uniaxial deformation; 4 – when deforming again to the initial deformation degree.

Figure 2. The spectra of X-ray luminescence of KBr crystal at 100K before and at low-temperature deformation (ε=1.5%) by crystallographic direction <110>. 1 – before deformation; 2 – at uniaxial deformation (100K); 3 – after removal of uniaxial deformation; 4 – when deforming again to the initial deformation degree.

It can be seen that the effect of amplifying the intrinsic luminescence of STE is clearly pronounced. However, at deformation by <100> direction, the σ-luminescence was the dominant luminescence (see figure 1), and at deformation by <110> direction, the dominant luminescence is radiation with a maximum at 2.95 eV with a large relative Stokes shift (SR=0.56).

In crystals KI and KCl, at deformation by <110> direction and in KBr crystal by <100> direction, no additional bands of radiation were detected besides to intrinsic σ-, π - luminescence. Regarding the nature of the emission band at 2.95 eV, it can be assumed that this is due to the luminescence of excitons localized near divacancies – e_{d0} (3.4 eV), vacancy quartets – e_{q0} (2.88 eV), or uncontrolled impurities [3]. However, in KBr crystal, large vacancy formations are created at high temperatures (300 K) by plastic deformation (ε=4÷6 %). If the radiation at 2.95 eV in X-ray spectra of KBr crystal is assumed to be associated with the quartet of the vacancies, then after the deformation is removed, the intensity of this radiation should remain unchanged, since the concentration of the previously created vacancy defects in the crystal remains constant with decreasing temperature. After the remove the deformation by <110> direction, at the same temperature (100K), the radiation intensity at 2.95 eV decreases sharply and only 10% of the intensity remains (figure 2, curve 3).

If we again resume the elastic deformation at 100K, the former values of the intensity, both σ– luminescence and luminescence at 2.95 eV are almost completely restored (figure 2, curve 4), that the effect is uniquely determined by the directed elastic deformation. There is also no reason to relate radiation at 2.95 eV with the luminescence of impurity excitons, since impurity luminescence completely disappears at deformation due to a shortening of the exciton free path to self-trapping near the impurity [4]. Since this radiation is characteristic of the intrinsic crystal lattice, it is reasonable to
explain its appearance as a result of the action of elastic deformation on different configurations of the STE.

Since the ratio between the radii of the anion and the cation for KI, KBr and KCl are 1.5, 1.9 and 2.2, respectively, then it is obvious that the size of the void containing the STE will be the largest for KCl and the smallest for KI. Therefore, in KI there are no configurational transformations of the STE, since its molecular core can not move.

For KCl, the conversion effect of STE configuration is possible, but in this crystal the luminescence of STE is already quenched at 40K. In KBr crystal a deformation by <110>, the core of STE is "pushed out" into the interstitial void. Thus, the STE is formed in a more asymmetric configuration than the "strong-off" (weak off), which corresponds to the emission band at 2.95 eV.

But in the spectra of the KCl crystal at deformation by <110> direction, in addition to the bands of intrinsic luminescence, no other bands are recorded, only in KBr crystal the uniaxial deformation has an orienting effect.

To explain the effect of the appearing of an excitons with more assymetric configuration only in KBr crystal we use the model of the configuration coordinates, according to which the changes in the exciton energy on the surface of the adiabatic potential correspond to the configuration transformations of the STE [5].

The total energy of the interacting electron-hole system in the adiabatic approximation can be written in the form of the following functional:

$$ E(\mu) = A\mu^2 - B\mu^3 - C\mu, $$

where $\mu$ – the ratio of lattice constant to the radius of self-trapping,

$$ A = \frac{3\pi\hbar^2}{2m_0a_0^2}, \quad B = \frac{E_d^2}{2\beta a_0^2}, \quad C = \frac{e^2}{\varepsilon a_0} $$

are the kinetic energy of the exciton, the deformation of the lattice when the volume is changed (it is assumed that the hole interacts with the acoustic lattice vibration), and the polarization of the lattice (in the interaction of the hole with the optical vibrations of the lattice). To determine the configuration transformations, we calculate the energies between the two states for the KI, KBr and KCl crystals. Since the energy in the functional 1 corresponds to the energy of the interacting "electron-hole" system, from the value of the difference between the two states, one can judge about the configurational transformations [6].

a) KI

For KI crystal the values $A=0.66$, $B=0.316$, $C=0.376$ [7]. The values $\mu$ for the initial configuration are calculated from the following considerations: $\mu=\alpha_0/a$, where $\alpha_0$ - lattice constant – 7.066 A; $a$– is the radius of self-trapping region. Since the STE in this crystal belongs to the "weak" configuration (figure 3), then for the radius of self-trapping region we take by geometric reasons the diagonal of the cube side of which is equal to the lattice constant, minus the radius of the halogen, since the configuration is weakly symmetric – 8.59 A. Then $\mu=0.82$.

Since the formation of an exciton with a strongly asymmetric configuration is impossible in this crystal, it is possible to form an exciton with a configuration that is less symmetric than "weak" (a shift of the molecular exciton nucleus to half the radius of the halide is possible), $\mu$ becomes 0.76. According to the functional, the energy difference becomes 0.0045 eV.

b) KBr

For KBr values $A=0.77$, $B=0.385$, $C=0.469$. The values of $\mu$ at initial configuration is calculated at $a_0=6.957$ A. Since the STE in this crystal belongs to the "strong-off" configuration (figure 4), as the radius of self-trapping region we take the diagonal of the cube side of which equal to the lattice constant – 9.82A. Then $\mu=0.7$.

Since in this crystal the STE already has a "strong-off" configuration, it is possible to form an exciton with a configuration that is less symmetrical than "strong-off" (the molecular exciton nucleus can be
displaced by half radius of the halogen), and μ becomes 0.66. According to the functional, the energy difference becomes 0.0016 eV.

Figure 3. The configuration of an exciton in KI. Figure 4. Configuration of an exciton in KBr.

c) KCl

For KCl values \( A = 0.63 \), \( B = 1.44 \), \( C = 1.11 \). The values of \( \mu \) at initial configuration is calculated at \( a_0 = 6.293 \) Å. Since the STE in this crystal belongs to the “strong-off” configuration (figure 4), as the radius of self-trapping region we take the diagonal of the cube side of which equal to the lattice constant – 8.89 Å. Then \( \mu = 0.7 \).

Since in this crystal the STE already has a “strong-off” configuration, it is possible to form an exciton with a configuration that is less symmetrical than “strong-off” (the molecular exciton nucleus can be displaced by half radius of the halogen), and μ becomes 0.69. According to the functional, the energy difference becomes 0.0232 eV.

As can be seen, the lowest energy is required for the configuration transformations in KBr crystal, the largest in the KCl crystal.

3. Conclusion

Thus, radiation at 2.95 eV with a large relative Stokes shift \( (S_R = 0.56) \) is characteristic for an STE with a strongly asymmetric configuration. Since the ratio between the radius of the cation and the anion in the KBr crystal is 1.9, which is much larger than in KI, its molecular core has the ability to shift. In KCl crystal, this process is also possible, but the luminescence of STE is already extinguished at 40K, so that no other luminescence bands are observed at deformation by \(<110>\) direction.

Therefore, this radiation is characteristic for the intrinsic crystal lattice and it is reasonable to explain its appearance as a result of the action of elastic deformation on various configurations of the STE.

This phenomenon of the appearance of the band at 2.95 eV at deformation by \(<110>\) direction only in KBr crystal is explained on the basis of the energy of excitons with different configurations on the surface of adiabatic potential for the KI, KBr, and KCl crystals. For KI, the configuration transformations require an energy of 0.0045 eV, KBr is 0.0016 eV, and KCl is 0.0232 eV. Since the lowest energy is in KBr, then there is a luminescence at 2.95 eV at deformation by \(<110>\) direction, associated with the luminescence of STE with less symmetric configuration than the “strong-off” (weak off).

References

[1] Shunkeev K Sh, Sarmukhanov E T, Barmina A A, Myasnikova L N and Shunkeev S K 2007 J.
Of Applied Spectroscopy 74 74

[2] Shunkeyev K, Sarmukhanov E, Barmina A, Myasnikova L, Sagimbaeva Sh and Shunkeyev S 2008 Phys. Solid State 50 1799

[3] Shunkeyev K, Sergeyev D, Drozdowski W, Brylev K, Myasnikova L, Barmina A, Zhanturina N, Sagimbaeva Sh and Aimaganbetova Z 2017 J. of Physics: Conference series 830 012139

[4] Lushchik A, Lushchik Ch, Vasil’chenko E and Popov A 2018 Low Temp. Phys 44 357

[5] Lisytsin V, Yakovlev V 1995 Phys. Tv. Tela 37 1126

[6] Shunkeyev K, Zhanturina N, Aimaganbetova Z, Barmina A, Myasnikova L, Sagymbaeva Sh and Sergeyev D 2016 Low Temp. Phys. 42 580

[7] Shunkeyev K, Sergeyev D, Myasnikova L, Barmina A, Zhanturina N, Shunkeyev S and Aimaganbetova Z 2014 Russ. Phys. J. 57 451