

## POLARIZATION OF SELF-ACTIVATED LUMINESCENCE IN ZnS CRYSTALS

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The polarization of luminescence in self-activated ZnS has been studied for two emission bands: 2.66 and 2.42 eV. It has been found that the orientation of luminescence centers responsible for the blue and green luminescence of self-activated (SA) ZnS crystals coincides with the three-fold symmetry axis. The centers of absorption and emission are systems composed (approximately) of linear  $\pi$  and a circular  $\sigma$  oscillators sharing respective parts  $\beta$  in the distribution of excitation and emission energy.

### 1. Introduction

The symmetry of luminescence centers and their orientation in ZnS crystals has been studied for years by many authors. There are many controversial views reported [2, 3, 6, 7] on this subject. It is usually assumed that the luminescence centers orientation in ZnS is along the two-fold or three-fold axis of symmetry. The radiation emission and absorption centers in ZnS are most probably the linear or circular oscillators. It is known that the two basic structures of ZnS (regular and hexagonal) create some tenths of polytypic structures of this compound [1]. Synthetic ZnS crystals constitute systems made of several polytypic structures. Assume that the orientation of the luminescence centers in crystals occurs along these crystallographic directions. It could be expected that the centers with identical properties will be differently oriented in a crystal. A useful method for investigating luminescence centers is the luminescence polarization diagram method. Recently, investigations of polarized luminescence of phosphors on the basis of ZnS have been the subject of numerous studies [2-11]. In this paper we concentrate on determining the orientation of centers responsible for blue (2.66) and green (2.42 eV) luminescence in SA ZnS crystals.

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## 2. Experimental method

The polarization diagram method worked out by Feofilov [12] and used mainly in investigations of polarized luminescence of regular crystals, is well known. It has been adapted in 1973 by Fok and coworkers [6, 7] for investigating the luminescence of a birefringening (uniaxial) crystal. The main idea of the method is the following: a parallelepiped slab is cut out of the crystals in such a way that the optical axis of the crystal is parallel to the slab along its walls. Luminescence in the slab is excited by linearly polarized light directed perpendicularly to the optical axis of the crystal. Position of the exciting electric vector is defined by an angle  $\varphi$  which the vector makes with the optical axis. Observation and measurement of glow is carried out along the excitation direction from the opposite side of the crystal. In the path of luminescence light an analyzer is placed. Two components of the glow intensity, parallel  $J_{\parallel}(\varphi)$  and perpendicular  $J_{\perp}(\varphi)$ , are measured for two positions of the analyzer with respect to the excitation vector. On the basis of these data, the polarization  $P(\varphi)$  is calculated from the formula

$$P(\varphi) = \frac{J_{\parallel}(\varphi) - J_{\perp}(\varphi)}{J_{\parallel}(\varphi) + J_{\perp}(\varphi)}$$

To account for the influence of birefringence on the polarization  $P(\varphi)$  and the shape of polarization diagrams, it is assumed that oscillators in the crystal are oriented along two, three and four fold symmetry axes of the crystal. It is further assumed that the directions of the oscillations do not change during the absorption and emission of energy. It means (approximately) that the spatial distribution of atoms (ions) around luminescence centers is uniform and does not depend on their state. According to Stoke's rule frequencies of emitting and absorbing are different. Coherence of excitation and luminescence radiation waves is therefore ruled out. It is known that after passing through a birefringening crystal, linearly polarized light becomes elliptically polarized. The parameters of the ellipse formed by the electrical vector loci change as the light passes through the crystal. Therefore, the propability of oscillators excitation will depend not only on their orientation, but also on their distance from the plane through which light enters the crystal. These oscillators, when excited, emit linearly polarized radiation which, due to birefringence of the crystal, changes into elliptically polarized. The parameters of this ellipse depend on location and orientation of the oscillators in the crystal. Luminescence light from oscillators of the same orientation will be only partially polarized. The coherence condition will not be obeyed because of the different depths of oscillators in the crystal.

In theoretical considerations the orientation of an oscillator has been characterized by a unit vector  $\mathbf{a}$  which at a distance  $y$  from the surface of the crystal has components  $(a_x, a_y, a_z)$  in an appropriate coordinate system  $Oxyz$ . The  $z$  axis has been chosen along the optical axis of the crystal, and the  $y$  axis along the direction of the exciting beam.

The exciting field  $E_w$  enforces the vibrations of an oscillator. The energy  $W$  of these oscillations is proportional to the mean square of the inner product of the field  $E_w$  and vector  $\mathbf{a}$

$$W \sim (E_w \mathbf{a})^2 = [a_x \sin \varphi \cos \Omega t + a_z \cos \varphi \cos (\Omega t + \delta_w y)]^2,$$

where  $\Omega$  denotes the frequency of the exciting,  $\delta_w y$  — phase difference between the orthogonal components  $E_{w_x}$  and  $E_{w_z}$  made on the path  $y$ . A dipole of energy  $W$  emits luminescence light of an amplitude  $E_l$  proportional to the  $\sqrt{W}$ . Vector  $E_l$  oscillates in the vector  $a$  and  $y$  axis plane. The luminescence light amplitude has the following components after emerging from the crystal:

$$E_{l_x} \sim \sqrt{W} a_x \cos \omega t; \quad E_{l_z} \sim \sqrt{W} a_z \cos [\omega t + \delta_l(l-y)],$$

where  $\omega$  is the luminescence radiation frequency,  $l$  — crystal thickness,  $\delta_l(l-y)$  — phase difference between  $E_{l_x}$  and  $E_{l_z}$  components acquired on the path  $(l-y)$ .  $\delta_w$  and  $\delta_l$  denote phase shift between the components  $E_x$  and  $E_z$  of the exciting and luminescence radiation, respectively, per unit crystal thickness.

Elliptically polarized light of intensity

$$i \sim W[a_x^2 \sin^2 \psi + a_z^2 \cos^2 \psi + 2a_x a_z \cos \psi \sin \psi \cos \delta_l(l-y)]$$

will pass through the analyzer located at an angle  $\psi$  with respect to the crystal optical axis. Due to noncoherence of the radiation from oscillators of a given orientation, we can integrate the above expression over the whole crystal thickness. The intensity of the luminescence light, per unit crystal thickness, is given by

$$J = \frac{1}{l} \int_0^l i(y) dy.$$

Assuming that  $\psi = \varphi$  and  $\psi = \varphi + 90^\circ$  we can calculate the parallel  $J_{\parallel}(\varphi)$  and perpendicular  $J_{\perp}(\varphi)$  components, as well as their sum and difference. If there are  $j$  different orientations in the crystal for equivalent oscillators, then one has to find for each orientation the sum and difference of the intensity components and then to integrate them over  $j$ . The expression for polarization  $P(\varphi)$  will take the form

$$P(\varphi) = \frac{\sum_j (J_{\parallel j} - J_{\perp j})}{\sum_j (J_{\parallel j} + J_{\perp j})}$$

under the assumption that there is neither decay, nor dichroism of the exciting and luminescence light. The influence of dispersion of birefringence on emission probability has also been neglected. As they differ only slightly, we have taken  $\delta_w = \delta_l = \delta$ . Theoretical polarization diagrams of luminescence corresponding to orientations of the centers along the two, three and four-fold symmetry axis are included in [7].

### 3. Experimental polarization diagrams of luminescence of self-activated ZnS crystals

Luminescence polarization of SA ZnS crystals obtained from the gaseous phase at  $1300^\circ\text{C}$  in an  $\text{H}_2\text{S}$  atmosphere, has been investigated. These crystals constitute systems of polytypic hexagonal and regular structures (specially in packing defected areas), and

therefore exhibit birefringence. Energy density distributions in luminescence spectra for these crystals have given in [11, 13]. To obtain experimental diagrams (for two emission bands 2.66 and 2.42 eV) equipment has been used similar to that described in [11]. Instead of monochromator UM-2, monochromator ZMR-3 has been used, and photomultiplier FEU-79 was substituted by EMI-9658. All experiments have been carried out at liquid

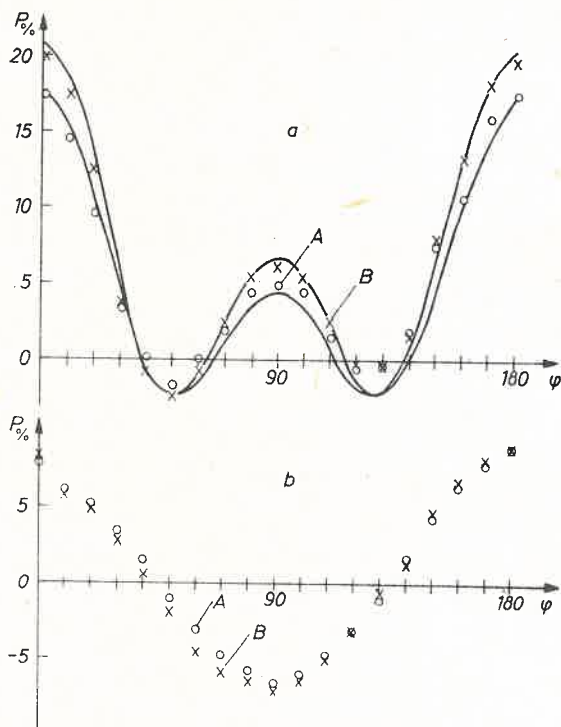


Fig. 1. Polarization diagrams for blue luminescence (2.66 eV) of *A* and *B* crystals excited by polarized (a) and unpolarized (b) UV radiation. Optical axis of the crystal coincides with the axis of the monochromator slit. The excitation direction is parallel to the tetrahedra symmetry plane. Solid lines represent the theoretical diagrams (for the *A* crystal:  $\beta = 0.4$ ,  $n = 1.55$ , and for the *B* crystal:  $\beta = 0.4$ ,  $n = 1.37$ ),  $\times$  and  $\circ$  are experimental curves

nitrogen temperature. The crystals have been ground and polished along natural growth planes parallel to their optical axes. Two crystals have been additionally ground along parallel to the optical axis and perpendicular to the growth planes. In this way, it has been possible to make polarization diagrams for two orientations of the crystals relative to the exciting beam and monochromator slit axis. In the first case, the direction of the exciting beam was parallel to the tetrahedron symmetry plane, and in the second (after rotating the crystal through  $90^\circ$  about the optical axis), it was perpendicular to the plane. Experimental polarization diagrams are presented in Figs 1, 2, 3, 4.

Fig. 1 presents polarization diagrams of two crystals *A* and *B*, made in the blue part of the 2.66 eV spectrum. The tetrahedron symmetry plane of these crystals has been parallel to the excitation direction. The optical axis has been parallel to the monochromator

slit. Fig. 1a shows the polarization of luminescence during polarized excitation of *A* and *B* crystals. In Fig. 1b we have the polarization of the same crystals but during unpolarized excitation by UV radiation.

In Fig. 2 the polarization curves of luminescence presented are for the same *A* and *B* crystals in the blue region of the 2.66 eV spectrum, obtained after rotating the crystals

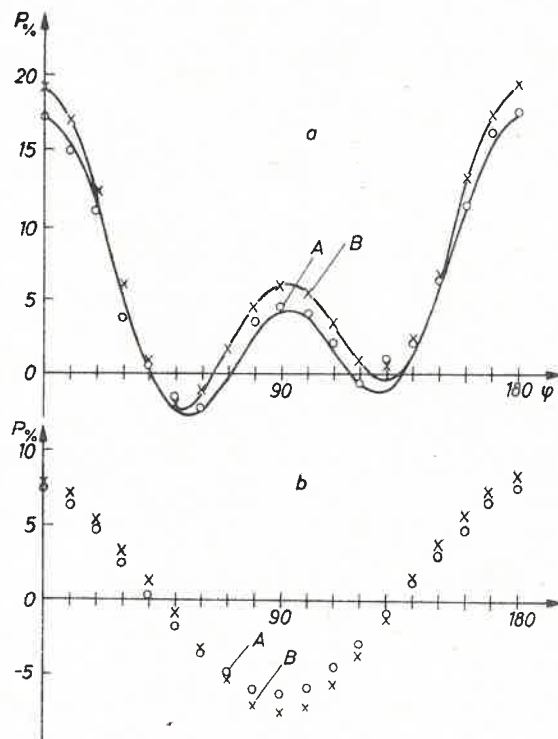


Fig. 2. Polarization diagrams for blue luminescence (2.66 eV) of *A* and *B* crystals excited by polarized (a) and unpolarized (b) UV radiation. Optical axis of the crystal coincides with the axis of the monochromator slit. The excitation direction is perpendicular to tetrahedra symmetry plane. Solid lines represent the theoretical diagrams (for the *A* crystal:  $\beta = 0.4$ ,  $\varkappa = 1.55$ , and for the *B* crystal:  $\beta = 0.4$ ,  $\varkappa = 1.37$ ),  $\times$  and,  $\circ$  are experimental curves.

by  $90^\circ$  about the optical axis. In Fig. 2a the crystals are excited by polarized UV radiation and Fig. 2b — by unpolarized radiation.

Fig. 3 presents the polarization diagrams of luminescence of *A* and *B* crystals obtained in the green part of the spectrum (2.42 eV). Crystal orientation relative to the monochromator slit and direction of exciting beam are the same as in the case illustrated in Fig. 1. Fig. 3a corresponds to polarized, Fig. 3b to unpolarized excitation, respectively.

Fig. 4 shows polarization diagrams of luminescence for two crystals *C* and *D* with optical axes perpendicular to the monochromator slit, and with the tetrahedral symmetry plane parallel to the excitation direction. These diagrams have been obtained in the blue region of the emission band (2.66 eV). Fig. 4a corresponds to the case when excitation

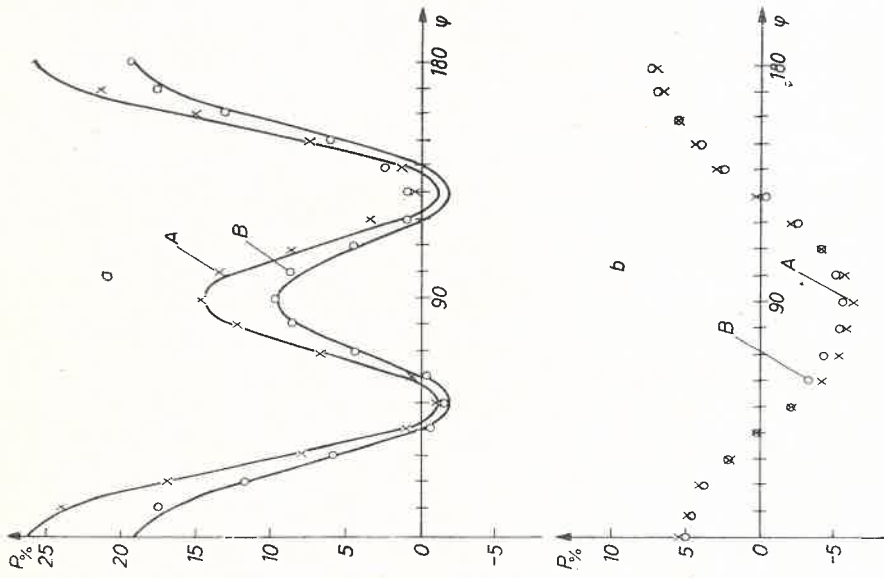


Fig. 3

Fig. 3. Polarization diagrams for green luminescence (2.42 eV) of *A* and *B* crystals excited by polarized (a) and unpolarized (b) UV radiation. Orientation of the crystals as in Fig. 1. Solid lines represent theoretical diagrams (for the *A* crystal:  $\beta = 0.27$ ,  $\alpha = 1.3$ , and for the *B* crystal:  $\beta = 0.34$ ,  $\alpha = 1.28$ ),  $\times$  and  $\circ$  are experimental curves

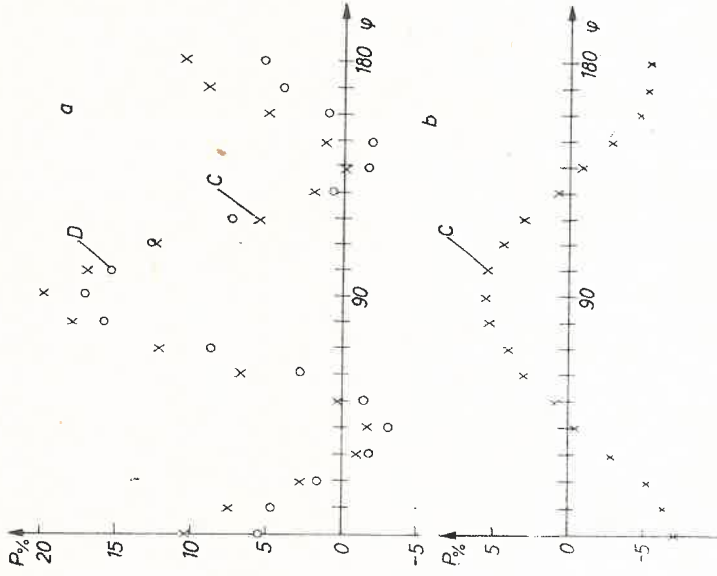


Fig. 4

Fig. 4. Experimental polarization diagrams for blue luminescence of *C* and *D* crystals excited by polarized (a) and unpolarized (b) UV radiation. Optical axis of the crystal is perpendicular to the monochromator slit. Excitation direction is parallel to the tetrahedra symmetry plane

is polarized, and Fig. 4b — when it is not. These diagrams show that as the crystal optical axis is rotated by  $90^\circ$  (perpendicular to the excitation direction) the reading of the angle  $\varphi$  changes which produces a shift of maxima from their location in Fig. 1a.

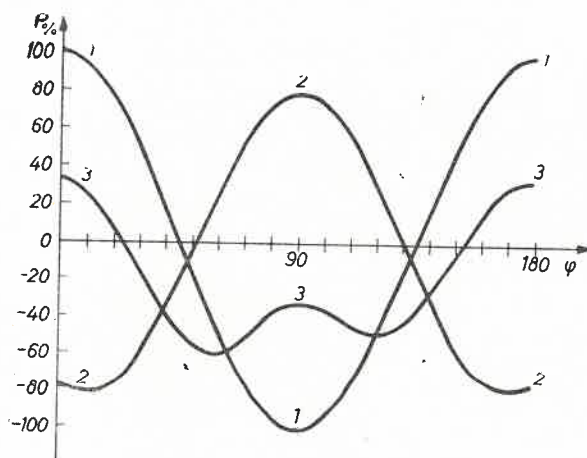


Fig. 5. Theoretical polarization diagrams from oscillators oriented along some of the two- and three-fold symmetry axes (see explanation in the text)

#### 4. Conclusion and final remarks

On the basis of the performed polarization measurements, we can state that in self-activating ZnS crystals the luminescence centers have a preferred direction of optical transitions. This is confirmed by the non zero value of the polarization  $P(\varphi)$  during unpolarized excitation, which has already been known before [3,11]. As in [3, 6, 7, 11] polarization diagrams obtained during linearly polarized excitation exhibit at  $P(0^\circ)$  and  $P(90^\circ)$  polarization maxima of different values. This fact alone, i. e.,  $P(0^\circ) \neq 0$ , strongly suggests that the centers responsible for blue and green luminescence of SA ZnS crystals are not oriented along four-fold symmetry axes. It is easily seen from Figs 1a, 2a, 3a and 4a that the respective polarization diagrams have asymmetric shapes. This asymmetry in polarization curves indicates that luminescence centers in crystals are located asymmetrically with respect to the plane made by the crystal optical axis and direction of observation. This asymmetry is made even more pronounced by the rotation of the crystal by  $90^\circ$  about the optical axis, as can be seen comparing Fig. 1a with 2a. Maximum values of the polarization for the investigated crystals oscillates between 17% and 26%, therefore it is 3 to 4 times smaller than the theoretical ones calculated for linear oscillators  $\pi$  (for  $\varphi = 0^\circ$  it is 62.5% for the orientation along two-fold axes and 75% — along three-fold ones). Polarization diagrams presented in Figs 1b and 2b and obtained during unpolarized excitation are similar. They correspond to the case when the tetrahedral symmetry plane is parallel and perpendicular to the excitation direction. Analysis of the theoretical diagrams (for the case parallel excitation) resulting from each of the four oscillators oriented along three-fold symmetry axes suggests that the two oscillators (one parallel to the optical

axis of the crystal, and the second lying in the tetrahedron symmetry plane) yield polarization curves similar in their behaviour to the experimental diagrams of Figs 1b and 2b. Curve 1 in Fig. 5 illustrates the polarization diagram of those two dipoles. Its shape does not depend on either the crystal thickness or on the phase shift  $\delta l$ . As compared to experimental curves, it differs significantly in the vicinity of extrema. The remaining two dipoles give different polarization rotation about an appropriate direction.

In [6, 7] a system consisting approximately of a linear  $\pi$  oscillator with a fixed axis and a plane oscillator  $\sigma$  (circular oscillator) spinning about this axis has been taken as an elementary center of absorption and emission in SA ZnS crystals. The excitation energy of such a system, not necessarily in a uniform way, between the dipole and rotator. To characterize the contribution of the rotator in the distribution of excitation and emission energies, a parameter  $\beta$  is introduced. The contribution of the linear oscillator is equal to unity. If  $\beta = 1$ , then the contributions of the rotator and dipole are equal. Taking the coefficient  $\beta$  into account one comes to the lowering of the theoretical value for  $P(\varphi)$ . However, the value of  $P(\varphi)$  at  $P(0^\circ)$  and  $P(90^\circ)$  are lowered by the same rate. The maxima of the experimental curves for  $\varphi = 0^\circ$  and  $\varphi = 90^\circ$  differ by a factor of two in their magnitude. One can obtain the observed difference between  $P(0^\circ)$  and  $P(90^\circ)$  if one assumes that in the crystal there are oscillators with preferred transitional directions. One can ascribe to these oscillators greater statistical weight  $\kappa$ . In the area of packing defects these should be the oscillators making large angles with the packing defect's plane. As it is shown by experiments with unpolarized excitation dipoles oriented along the crystal optical axis may serve as an example of such oscillators. Respective expressions for polarization  $P(\varphi)$  in which both  $\beta$  and  $\kappa$  have been taken into account are given in [7]. By comparing, at points  $P(0^\circ)$  and  $P(90^\circ)$ , the theoretical and experimental results, we get two sets of equations from which  $\beta$  and  $\kappa$  can be determined. It follows from [6, 7] that for SA crystals the phase shift  $\delta$  is about  $1000^\circ/\text{mm}$ . If one knows the thickness  $l$  of the crystal, one can estimate  $\delta l$ . To obtain the experimental value of  $\cos \delta l$  the same equipment has been used as for measuring the polarization  $P(\varphi)$  of luminescence. Solid lines in Figs 1a, 2a, 3a represent theoretical polarization diagrams corresponding to orientation of the oscillators along the three-fold symmetry axis, and with  $\beta$ ,  $\kappa$ ,  $\cos \delta l$ ,  $\sin \delta l$  taken into account. As it is seen from Figs. 1a, 2a, 3a, there is satisfactory agreement between experimental and theoretical results. The existing discrepancy lies within the experimental error which increases if the optical axis of the crystal is not exactly orthogonal to the excitation direction. Polarization diagrams of luminescence from oscillators oriented along the two- and three-fold symmetry axes are similar, differing only in  $P(\varphi)$  values. Experimental  $P(\varphi)$  values are always smaller than the respective theoretical ones. It is, therefore, rather difficult to establish if a particular diagram belongs to a group of diagrams corresponding to two-fold or three-fold symmetry axes. Fok and coworkers [7] have introduced characteristic parameters  $S_1$  and  $S_2$  permitting classification of experimental diagrams into a group of diagrams of appropriate orientation. The parameters  $S_1$  and  $S_2$  do not depend on  $\beta$  and  $\delta l$ . For oscillators oriented along two-fold axes  $S_1 = 23$  and for three-fold  $S_1 = 11$ . For the  $S_2$  parameter we have  $12/11$  and  $6/5$ , respectively. It can easily be shown that the parameters  $S_1$  and  $S_2$  have the



same value, whether the crystal is excited parallelly or perpendicularly to the tetrahedral symmetry plane. They depend, however, on the statistical weight  $\kappa$ . If one accounts for the coefficient  $\kappa > 1$  in theoretical expressions, then the value of  $S_1$  and  $S_2$  will decrease. From the measurements of  $S_1$  and  $S_2$  we have carried out, it follows that  $S_1 = 4.8$  and  $S_2 = 1.12$ . As one can see, these values are closer to the theoretical estimations for  $S_1$  and  $S_2$  and for orientation of the oscillators corresponding to three-fold symmetry axes.

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