Acta Physica Universitatis Comenianae
Vol. XLVI–XLVII, (2005–2006) 101–108

Influence of Stacking Disorder on the Optical Properties of Layered Crystals GaSe

A. G. Kyazym-zade[1], A. Mokhtari[1], I. Hympanova[2], V. M. Salmanov[1], Yu. Asadov[1], A. A. Agaeva[1]

[1]Baku State University, Z. Khalilov str. 23, 370145 Baku, Azerbaijan, E-mail: *vagif_salmanov@yahoo.com*
[2]Faculty of Mathematics, Physics and Informatics, Comenius University, 84248 Bratislava, Slovak Republic

Abstract: The influence of stacking disorder on the optical properties of layered GaSe crystals is discussed. X-ray analyses show that GaSe crystals grown with Bridgman method consist of a mixture of two modifications ( ). In sample of -modification part, anomalous refraction by one of various lights is observed (He-Ne, Dye, YAG: Nd^{+3} lasers and collimated beam). The incident light is perpendicular to the surface of the sample; contrary to passing always along the incoming direction, it splits to two parts making angles of 13 and 70 . In transmission and photoconductivity spectra of the -modification, free exciton absorption exists, whereas this peak is absent in these spectra in -modification part samples. In thin film GaSe, which is obtained by thermal evaporation method and is sprayed under a corner, laser beam is also refracted anomalously. Besides, the high photovoltage (~30 V) is observed in these films. The result of the measurements on GaSe indicates that the mentioned properties are explained by stacking disorder of the layers.

1. Introduction

Gallium selenide is a layer semiconductor of the III-VI family, where each layer contains two gallium and two selenium close-packed sub-layers in the stacking sequence Se-Ga-Ga-Se [1]. The bonding between two adjacent layers is of the weak Van-der Waals type, while the bonding is predominantly covalent within the layer. The optical c-axes of crystals are orthogonal to the layers, having thicknesses of 0.8 nm [2]. Depending on the packing of the layer, various modifications are formed (and), in which the position of band edge is determined by interlayered interactions. The real crystals of the compounds are often represented in form of a mixture of various modifications, in which the violation of layers joint characters on the boundaries of separate modifications occurs. Besides, the weakness of interlayer bonding practically always results in a displacement of group of layers against each other and self-organization of packing defects. Such self-organized defects of packing results, in turn, in violation of periodicity of the potential along the crystallographic c-axis and an additional one-dimensional fluctuating potential in this direction acts on the crystal. It has been shown that the stacking disorder present in layer crystals GaSe has a strong influence on the electronic, photoconductivity properties and Wannier excitons [3 8]. The experimental results for the DC dark conductivity, which was measured for GaSe, show a strongly temperature-dependent anisotropy

$$_{||} / \quad A\exp(\quad E / kT),$$

where $_{\parallel}$ and describe the conductivity parallel to or perpendicular to the crystallographic c axis, respectively. A is of the order of the effective-mass ratio of the holes m /$m_{\parallel}$ = 4 and E is the sample-dependent parameter of the order of 10 100 meV. It is found, that in the presence of stacking disorder, the excitons are confined to a finite number of layers. The absorption spectra GaSe turn out to be strongly sample dependent. The variety of absorption spectra observed in GaSe can be related to the different stacking orders occurring in this material.

In the present paper influence of stacking disorder on the optical properties GaSe has been investigated experimentally. Therefore, in this work, we grew this crystal by the Bridgman technique, analyzed its structure by the X-ray method, measured the transmission and photoconductivity spectra and finally, we studied the influence of stacking disorder on these parameters.

2. Experimental Procedures

The investigated crystals GaSe were grown by the Bridgman method. Kernels Ga and Se (with purity of 4 orders) with accuracy of 1 milligram have been taken in stoichiometric ratio. At first kernels Se and then Ga have been shattered and filled in a quartz ampoule. The ampoule has been pumped out, sealed and placed into the electric heater. In the beginning, at a temperature ~50 C, the ampoule with initial substances was maintained for about 1 hour. Then the temperature was increased up to 255 C and the substance maintained at this temperature up to 30 minutes and the substance was automatically mixed during this time. Furthermore, during two hours the temperature in the furnace was increased up to 1000 C and, at this temperature, the maintained liquid melt and it was mixed with an electric motor within 3.5 hours. Then the mixer was turned off and the substance maintained for ~ 0.5 hour.

A crystallization cycle of the syntheses was performed at a very slow speed of cooling. In spite of the fact that there were no traces of reacting components on ampoule walls after synthesis, the next day synthesis process was repeated in the same ampoule, but with the difference, that until reaching the temperature 1000 C no process of endurance was made at the certain temperatures. But at 1000 C the liquid was melt again during 3.5 hours and maintained by the electromotor for mixing. Polycrystalline GaSe obtained on the basis of such technology was layered and completely pure. Then this polycrystal was cut into very small particles and also filled in a quartz ampoule with the conic end in order to grow monocrystalls from it by the directed crystallization method. The temperature of the hot zone (top) was 1050 Cand the temperature of the cold zone (bottom) was 800 C. In the hot zone the ampoule, together with the substance, was maintained for about 3 hours. Then electromotor for movement of the ampoule was turned off and the growth rate of crystals was 4 mm/hour. With such a speed the ampoule passed a distance about 21 cm within 48 hours, passing from the hot zone to the cold crystallization zone. After switching-off both heaters, movement of the ampoule with substance proceeded for about next 5 hours. Thus, crystal GaSe with weight of 15g, diameter 10 mm and length 20 cm has been grown. Samples were obtained by cleaving the ingots along the plane of the layers into slices about 1 cm^2 and with thicknesses of a few micrometers. For checking reproducibility of observable effects, synthesis and cultivation of crystals was repeated for many times in the same experimental con-

ditions. This was the possibility how reception of identical results in many samples was shown.

Thin films GaSe were obtained from thermal evaporation in vacuum 6×10^{-5} mHg. This process was made under angle ~ 80° to the substrate. The thin films were rendered on the polished glass substrates heated up to 150°C. Thicknesses of the thin films were about 0.5÷4.6 m. The contacts In, Ga were rendered on the film for the research.

As a source of radiation the following has been used: continuous gas laser He-Ne (= 632.8 nm, W = 1mW), pulse solid laser YAG: Nd^{3+} (= 1060 nm, W = 1MW/cm^2, t = 10 ns), pulse liquid laser (Rodamine 6G dye laser) tuned through the region (= 594÷643 nm, W = 120 kW, t = 1÷3 ns) and also the collimated beam from a natural source. Laser beam intensity was varied by insertion of calibrated neutral density filters. The incident light being perpendicular to the layer surface (parallel c-axis) was focused into a spot of 0.1 mm. Optical and photoelectrical measurements were carried out with the use of non-stationary digital system (transient digitizer system), in which the silicon photodiode is included, suitable for the use of such a type of the laser measurements, a memory oscillograph (Le Croy 9400) and a computer system (board Master 800 ABI 8).

3. Experimental Results and their Discussions

At first we prepared samples from GaSe crystals with area about 1 cm^2 and thickness 200 m. The laser or collimated beams were directed perpendicularly to crystal layers and then their passage was refracted with angle about 13 . Rotation of the crystal around the beam and in other directions has shown that it behaves similarly to a prism (Fig. 1).

With further spalling, thickness of samples has been reduced up to 100 m, however, the angle of a deviation still remained about 13°, and at last, it was possible to prick out a sample thickness not less than 3 5 m. However, the angle of deviation remained about 13° with this thin sample. It is specified that the observed anomaly was apparently located in several monolayers of crystal GaSe. We have prepared also such a sample, in which the "normal" and "anomalous" parts are together, so make us possibility to compare their each other. X-ray analysis of a "normal" and "anomalous" parts is shown in Fig. 2. We showed the detail of our calculation concerning these two parts in Tables 1 and 2.

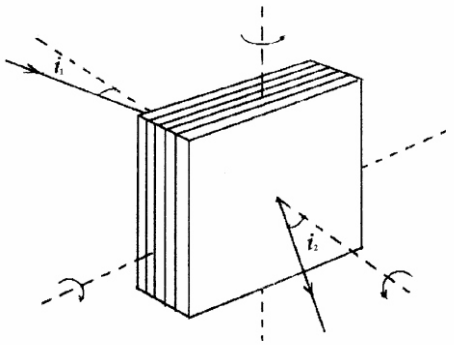

Fig. 1. Rotation of crystal around the beam and other directions.

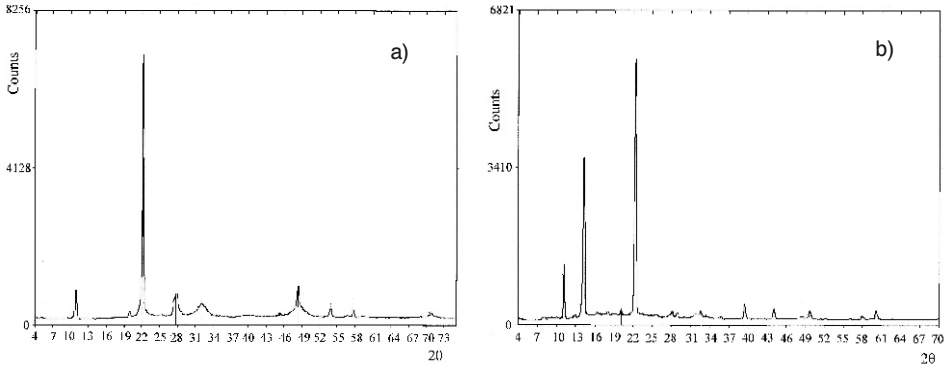

Fig. 2. Difractogramms for "normal" (a) and " anomalous " (b) parts of GaSe.

Table 1. Calculated parameters for "normal" part GaSe by X-ray analysis.

№		I/I_0	$d_{exp.}$(nm)	$d_{calc.}$(nm)	hkl
1	5 33′	60	0.79721	0.79801	002
2	10	1	-	-	-
3	11 08′	100	0.39922	0.39901	004
4	13 58′	10	0.31948	0.31920	005
5	16 00′	6	0.27972	0.27847	103
6	24 16′	15	0.1875	0.18875	110
7	27 06′	5	5 .16924	0.17062	114
8	27 0′	4	0.15984	0.15960	0010
9	35 30′	4	0.13275	0.13300	0012

Table 2. Calculated parameters for " anomalous " part GaSe by X-ray analysis.

№		I/I_0	$d_{exp.}$(nm)	$d_{calc.}$(nm)	hkl
1	5 32′	20	0.79969	0.79975	004
2	7 00′	80	0.63240	0.6398	005
3	8 30′	6	0.52158	0.53317	006
4	10 00′	8	0.44407	0.45700	007
5	11 11′	100	0.39758	0.39988	008

6	14 05′	3	0.31685	0.31990	102,0010
7	14 28′	2	0.30861	0.31099	103
8	16 43′	2	0.26795	0.26658	0012
9	19 45′	20	0.22694	0.22804	1010
10	22 03′	20	0.20535	0.20615	1012
11	24 53′	10	0.18324	0.18279	114
12	28 59′	5	0.15911	0.15933	204
13	30 04′	10	0.15387	0.15350	1112

These analyses show that “normal” indicated part was related to hexagonal -modification of GaSe with the lattice constant a = 0.37751 nm, c = 1.59602 nm and “anomalous” indicated part was related to hexagonal -modification of GaSe with the lattice constant a = 0.37493 nm, c = 3.15798 nm (see Table 3). It is noted that the calculated lattice constants are in good agreement with the lattice constants which are in [9, 10].

Table 3. Polytypes of GaSe crystals [11].

Modification	**Space group**	**a**, nm	**c**, nm
- GaSe	D^4_{6h}	0.375	1.594
- GaSe	D^1_{3h}	0.373	1.588
- GaSe	D^5_{3v}	0.373	2.386
- GaSe	D^4_{6v}	0.375	3.199

A careful analysis of a direction and sizes of deviation angle i_2 from the size and the direction of incidence angle i_1 has been conducted with the help of precision goniometer (Fig. 3). The incidence angle i_1 varies from +45 up to 45 concerning the axis of normal fall. Curve 1 was received at such orientation of crystal, when the falling and rejected beams lay in a plane perpendicular to planes of supervision. Curve 2 was received after the turn of a crystal around a falling beam by 180 . As it is seen from Fig. 3, while changing the incidence angle from +25 to 25 , the angle of deviation practically remains constant, about 12 50 Only at falling angles bigger than 40 (curve 1) and +40 (curve 2) the deviation angle starts to increasing appreciably.

Besides, we observed also the second refracted beam with angle about 70 whereas its intensity was essentially weaker in relation to the first refracted beam (curves 3 and 4 in Fig. 3). As it is seen from the figure the deviation angle also poorly depends on an angle of falling.

Transmission spectrum of one of the investigated samples from “normal” and “anomalous” parts of a crystal is shown in Fig. 4. It is seen that in a “normal” part the exciton

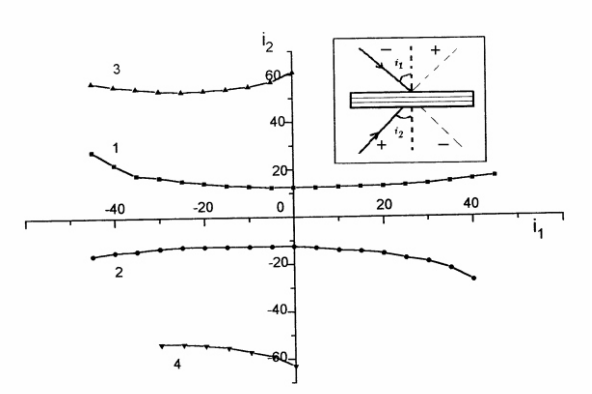

Fig. 3. Dependence of deviation angle i_2 on the incidence angle i_1. The inset shows the incident (i_1) and deviation (i_2) beams schematically.

peak with wavelength = 620 nm is observed and this peak is absent in an "anomalous" part of a spectrum. It is noted that exciton binding energy is equal to 20 meV, which is close to the room temperature thermal energy (kT = 26 meV at 300K) [12], therefore, we can observe the exciton peak in GaSe at room temperature. Exciton peak is also observed in "normal" part in the photoconductivity spectrum GaSe (Fig. 5, curve 1), but this peak is absent in "anomalous" part samples. In "anomalous" part, instead of exciton peak, the low-energy peak with a maximum 1.96 eV appears in the spectrum, most likely due to impurity center with depth deposition ~0.26 eV (Fig. 5, curve 2) [13].

Absence of appreciable polarization at both rejected beams specifies that we do not deal with two-refraction or dichroism. Deformation compression of layers at extraction of crystals from an ampoule is improbable, as we carried out special mechanical influences on final the parts of specially selected samples.

For the He-Ne laser ray with wavelength = 630 ÷ 650 nm, the deviation angle was 12°50 and for YAG: Nd^{3+} laser with wavelength = 1060 nm this angle was 11°45 . Thus the angular dispersion was D = 2.5 angular unit/micron. If the optical system has a focal length about 50 cm, then the linear dispersion is D* = 47 nm/mm, that is comparable to parameters of good optical devices. Thus, it is clearly that application of GaSe crystals as spectral devices, especially in infra-red region, becomes perspective.

It is possible, analyzing all the set of experimental data, to assume that the possible reason of anomalous refraction of light in crystals GaSe is the presence of a plenty of defects of packing in them, which can lead to a strong deformation of potential between the layers. As a result, group of layers, instead of usual, strictly perpendicular arrangement to an optical c-axis, will form some angle with it. The reason of this phenomenon might be, in particular, the presence of a gradient of temperature during cultivation of a crystal. This fact testifies, for the benefit of the given assumption, that rotation of a crystal around a beam and in other directions has shown that they behave similarly to an optical prism. Estimations show that the behavior of the outcoming beams is similar to that of the refracted rays from a prism made of GaSe with refraction angle 7 and refractive index equal to 2.8 [14]. The optical scheme of experiment of the "anomalous" refraction of light in a GaSe layered

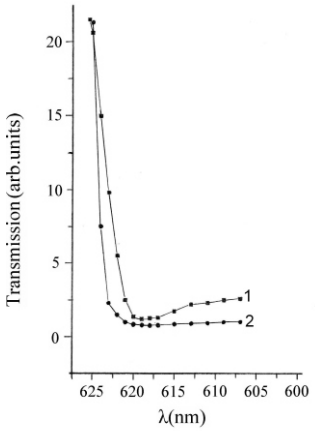

Fig. 4. Transmission spectra of GaSe for (1) and (2) modifications.

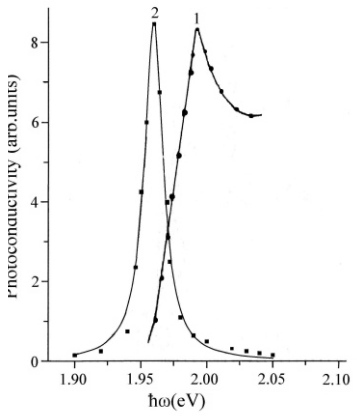

Fig. 5. Photoconductivity spectra of GaSe for (1) and (2) modifications.

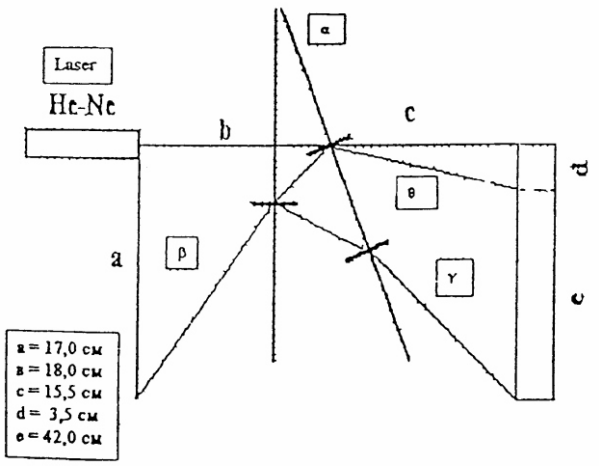

Fig. 6. The optical scheme of experiment of the " anomalous " refraction of light in GaSe layered crystal.

crystal is shown in Fig. 6. It is seen from the figure that a He-Ne laser light is directly perpendicular to the surface of the samples, instead of propagation along direction of the incident light, it splits (without dispersion) into two parts with angles of 13° ( ) and 70° ( ) in relation to the direction of incident light.

Intensity of the second beam (reflected under the angle 70) is rather lower than that of the first one. Value of angles , and specified in the figure coincide well with the experimentally found values.

One more proof of formation of natural prisms in layered crystals GaSe during their growth are the experiments held with a thin film sprayed under an angle of these crystals. At a laser beam with wavelength of = 632.8 nm falling normally to a surface film GaSe, incident beam deviates by 40 concerning the direction of the beam. In this thin film GaSe, alongside with anomalous refractions of light, a high photovoltage ~30V is also observed. It is not accidental, as it is known that the sprayed film under an angle produces a more photovoltage, apparently, by amplification of heterogeneity and increases in porosity, as well as greater sensitivity of such films to influence adsorption.

It is known that appearance of the high photovoltage in the thin films can be explained by the model, according to which this voltage is formed from series-connected transitions or in other photocells, and it is formed as a consequence of bend zone junction between oriented crystallite.

In many films, photocells are formed with repeated series defects of packing. It is possible to assume, based on the data on kinetic increase and relaxation of a photovoltage in the films GaSe, that the high photovoltage is created by a spatial charge which arises because of nonuniform distribution of the nonbasic carriers seized on structural defects.

4. The Conclusion

We have shown that stacking disorder has an influence on the optical properties in layered GaSe. The observed anomalous refractive effect can be explained by making angles between the layers, which lead to formation of a natural prism into samples. Crystals GaSe are convenient objects for making the spectral devices on the base of their micron thickness with a good dispersion in parameters. Thin film GaSe sprayed under an angle, possesses a high photovoltage that shows its perspectives in photovoltaic transformations.

References

[1] M. Schluter: Nuovo Cimento B **13** (1973) 313.
[2] I. M. Catalano, A. Cingolani, M. Ferrara, A. Minafra: Phys. Stat. Sol. (b) **68** (1975) 341.
[3] K. Maschke, Ph. Schmid: Phys. Rev. B **12** (1975) 4312.
[4] K. Maschke, H. Overhof: Phys. Rev. B **15** (1977) 2058.
[5] J. J. Forney, K. Maschke, E. Mooser: J. Phys. C: Sol. Stat. Phys. **10** (1977) 1887.
[6] Z. T. Kuznicki, K. Maschke, Ph. Schmid: J. Phys. C: Sol. Stat. Phys. **12** (1979) 3749.
[7] A. G. Kyazym-zade, A. Z. Abasova, V. M. Salmanov, L. G. Gasanova, A. G. Mamedova: Mater. Science and Engineer. B **88** (2002) 282.
[8] A. G. Kyazym-zade, V. M. Salmanov, I. Hympanova, A. A. Agayeva: Acta Phys. Univer. Comen. **XLIII** (2002) 61.
[9] A. Kuhn: Acta Crystallogr. B **31** (1975) 2841.
[10] M. Anis, J. Nazar: J. Mater. Sci. Lett. **2** (1983) 471.
[11] G. A. Belenkiy, V. B. Stopachinskiy: Uspekhi Fiz. Nauk **140** (1983) 233.
[12] J. M. Besson, K. P. Jain: Phys. Rev. Lett. **32** (1974) 936.
[13] G. B. Abdullaev, G. L. Belenkiy, S. M. Rivkin, Y. P. Sharonov, V. M. Salmanov, I. D. Yarosheskiy: Fiz. Tekh. Poluprovodn. **5** (1971) 374.
[14] Le Toullec: Nuovo Cimento **38** B (1977) 159.