

OPTICAL SPECTRA OF HEXAGONAL SELENIUM SINGLE CRYSTALS GROWN FROM THE MELT UNDER HIGH PRESSURE (PART II)

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The reflection spectrum of single crystals of hexagonal selenium grown up from the melt under high pressure in beam energy interval 1-6eV normally incidence on the surface is investigated. The spectral dependences of optical constants and dielectric functions are calculated by Kramers-Kronig method. The optical transitions are confirmed in samples under consideration in photon energy region 1÷6 eV.

Keywords: selenium, single crystal, reflection spectrum.

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INTRODUCTION

The electron properties of selenium crystals are studied in series of works [1-17]. The authors [18,19] have synthesized the reflection spectrums of selenium crystals in region 0-30 eV obtained at usual conditions on the base of reflection spectra. They note that the coincidence of experimental and theoretical functions gives the possibility to make the quantum leap in formation of deep and total nature scheme of inherent energy levels and transitions between them under the influence of different external factors (photons, temperature, pressure, electric and magnetic fields and etc).

The obtaining of selenium single crystals at usual conditions is conjugated with big difficulties which are connected with peculiarities of its crystallization. This doesn't allow us to obtain its crystals in big sizes and high purity. However, at high pressures (~4,5 kbar) these disadvantages aren't revealed [23]. The crystal optical spectra grown up under the pressure are studied in the given work.

Note that it is necessary to know the solid substance electron structure, i.e. the dependence of electron energy on wave vector in different energy bands $E_n(k)$ and mutual band positions for revealing of conduction electron movement peculiarity confirming the character of many experimentally observable phenomena. The knowing the electron structures of semiconductors allows us to directly use and change their properties.

It is necessary to note that all empirical calculations of band structure are mainly based on data of optical measurements [24,25]. The experimental data are often used for refinement of theoretical calculation results.

The interaction of the light with substance is described by refraction index and absorption coefficient k which characterize the phase and damping of plane wave in substance. These values can be confirmed from the measurements of substance reflection coefficients which are confirmed on reflected light phase from Kramers-Kronig formula:

$$\theta(E_0) = \frac{E_0}{\pi} \int_0^{\infty} \frac{\ln R(E)}{E_0^2 - E^2} d\omega,$$

$$n = \frac{1 - R}{1 + R - 2\sqrt{R \cos \theta}}, \quad k = \frac{-2\sqrt{R \sin \theta}}{1 + R - 2\sqrt{R \sin \theta}}.$$

The rest optical parameters are calculated by n and k values and by formulae alternative from them.

It is necessary to take into consideration the influence of whole spectrum region on reflected light phase for its confirmation from the measurements of reflection coefficient $R(E)$. The extrapolation method $R(E)$ on whole unmeasured spectrum region is used by us.

The procedure of semiconductor optical parameter confirmation on the base of experimental data by reflection is expressed in [26]. Moreover, it is necessary that its optical parameters are confirmed in whole region of interband transitions.

It is necessary to note that values of interband transitions for the given material depend on crystallographic directions.

As author mentions [27], only one reflected wave appears at reflection into transparent medium, wave vector is confirmed definitely, independently on surrounding medium properties. At n and k are confirmed by complex formulae at beam oblique incidence on the surface. However, these formulae simplify at normal incidence. ε , k and σ parameters at beam reflection in anisotropic mediums have tensor character that is conjugated with significant math difficulties but the general situation keeps the same and the crystal behaves itself as isotropic medium at chosen directions and orientations. However, it is necessary to specially choose the more profitable orientation of crystallographic axis relatively beam surface for more clear revealing of its anisotropy and measurement of corresponding constants.

Thus, the reflection measurement for anisotropic mediums can give whole information on constant values and besides, serve for confirmation of axis orientation in crystal, orientation of reflecting surface, crystal symmetry and etc.

The reflection plays the big role in series of natural phenomena. The perspectives of light reflection application known today for investigation of composition and structure of substance and physical processes taking place in them have the exclusive importance if the information can't be obtain by other way [27].

The semiconductor optical functions in wide region of fundamental absorption are more effectively studied by the method of almost normal mirror reflection as it is mentioned in [28]. The other clearly optical methods have the essential principle or methodical limits and give the information in limited spectral regions adding the results for almost normal reflection and confirmation at necessity of interband transitions.

As it is mentioned in [29], the less symmetry of anisotropic crystals makes strongly difficult the confirmation of interband ridge displacement in Brillouin band, however, the many ridges form in high symmetry points and they don't reveal the significant dependence on polarization.

The wurtzite hexagonal structure, Brillouin zone of which has 32 symmetry elements and also ZnS (cubic and hexagonal structure) are totally studied from noncubic ones. As author [30] mentions, the zone structure of hexagonal crystals by wurtzite type in points $k=0$ in space along hexagonal axis can be obtained with the help of perturbation theory on corresponding zinc blende. The measurement of their reflection coefficients with non-polarized light shows that their spectra are similar ones and the insignificant shifts in position of first absorption edge from 0,02 up to 0,03 eV are observed at measurements in different directions of linearly polarized light in relation to crystal hexagonal axis.

The reflection spectra at normal light incidence on surface of cubic ZnS and structures by wurtzite type ZnS, CdS, CdSe in nonpolarized light are studied in [31]. Moreover, the distribution directions of incident light either parallel or perpendicular to "c" crystal axis. In first case the results are well coincide with author data for the case of polarized light in $E \parallel c$ direction and in second one the peaks become less at nonpolarized light.

The investigation of electron structures of anisotropic materials is studied by method of normal incidence at nonpolarized beam in [31-37].

The measurement is carried out at polarized light [33, 35] in several cases for confirmation of ridge displacement in Brillouin zone because of spin-orbit splitting. Usually, the optical parameters in both anisotropic and isotropic materials are confirmed from reflection measurements by method of nonpolarized light normal incident and ridge refinement is carried out with the help of measurement at polarized light in some cases.

The measurement of reflection coefficient $R(E)$ and confirmation of optical parameters of hexagonal selenium single crystals grown up from the melt under high pressure are the aim of the given work.

THE INVESTIGATION TECHNIQUE

The technique of selenium single crystal obtaining under high pressure is described in [23]. The selenium single crystals in ingot form by diameter 1cm and length 4 cm are obtained from the melt under pressure 4,5kbar. At this pressure the crystal growth rate increases in $\sim 10^3$ relatively to usual condition because of selenium chain shortening in the melt and decrease of crystallization centers under pressure. The sample crystallographic directions are roentgenographically confirmed.

For sample preparation the material piece is cut off, the surface of which is polished by vibration arrangement or by hand, later it is electrolytically etched in mixture from 5 parts NaOH (10% in water) and one part of tartaric acid (40% in water). After it, the sample surface is treated by etching of impulse current by density ~ 500 mA/cm².

$R(E)$ measurements are carried out in beam energy interval 1÷6 eV normally incident on sample surface. The optical parameters are confirmed by technique of work [26] with the help of special computer programs applied in series of works [38-47].

It is known that according to Maxwell equation all optical parameters are interconnected that is seen from the ratio:

$$\frac{\omega^2}{\nu^2} = \frac{\mu}{c^2} 4\pi\sigma(i\omega) + \frac{\mu\epsilon}{c^2} \omega^2,$$

where ω is cyclic frequency, c is speed of light in vacuum.

THE RESULTS AND THEIR DISCUSSION

$R(E)$ reflection is measured in work and the optical functions are confirmed on its base. Such parameters as: θ reflected light phase; κ absorption and n refraction indexes; real ϵ_1 and imaginary ϵ_2 parts of dielectric constant; α absorption coefficient; the function of characteristic volume $-Img \epsilon^{-1}$ and surface $-Img(\epsilon+1)^{-1}$ electron losses; electro-optical differential functions (α, β); $\epsilon_2 E$ optical conduction; $\epsilon_2 E^2$ integral function of bound state density; effective number of valent electrons $N_{ef}(E)$ by $-Img \epsilon^{-1}(E)$ and $-Img(\epsilon+1)^{-1}(E)$; $\epsilon_{0,ef}(E)$ effective static dielectric constant, $N_{ef}(E)$ effective number of valent electrons taking part in transitions up to the given energy E are obtained.

R reflection coefficient; electro-optical differential functions (α, β); $\epsilon_2 E$ optical conduction; $\epsilon_2 E^2$ integral function of bound state density; effective number of valent electrons $N_{ef}(E)$ by $-Img \epsilon^{-1}(E)$ and $-Img(\epsilon+1)^{-1}(E)$; effective static dielectric constant $\epsilon_{0,ef}(E)$; effective number of valent electrons $N_{ef}(E)$ taking part in transitions up to the given energy E are presented on fig.1-7 from obtained results.

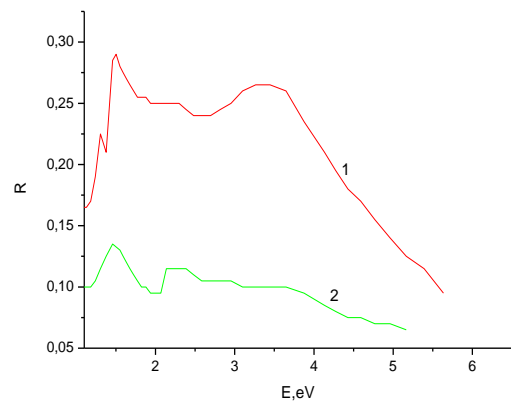


Fig.1. $R(E)$ reflection spectra of hexagonal selenium single crystals which are parallel (curve 1) and perpendicular (curve 2) to "c" axis.

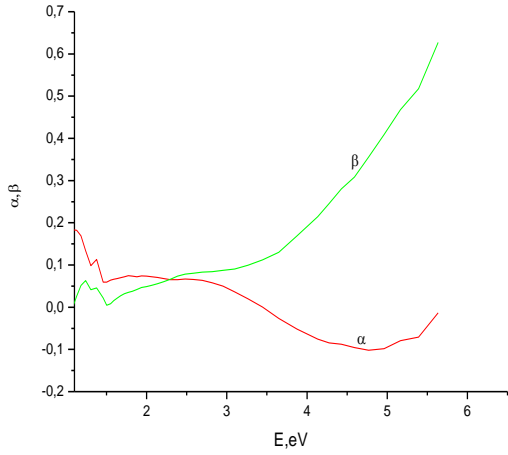


Fig.2. The spectra of electro-optical differential functions (α, β) of hexagonal selenium single crystals parallel to “c” axis.

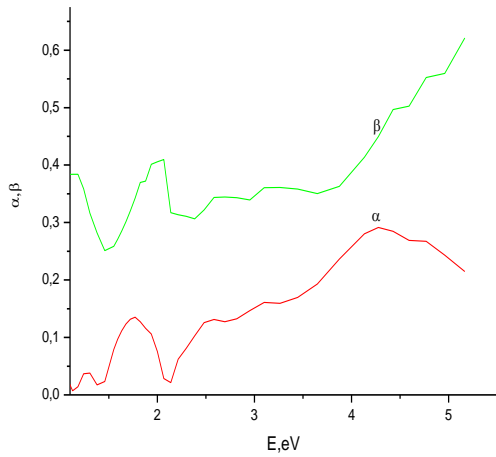


Fig.3. The spectra of electrooptical differential functions perpendicular to “c” axis.

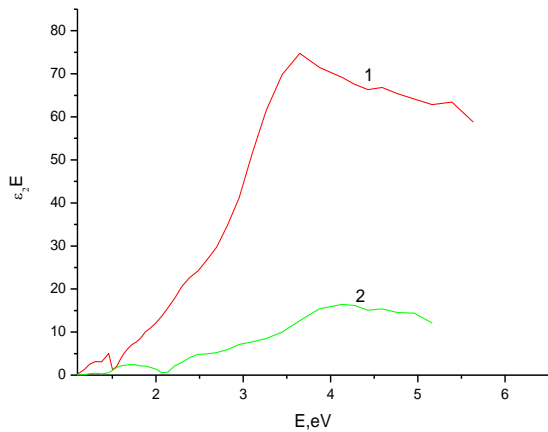


Fig.4. The spectra of $\epsilon_2 E$ optical conduction of hexagonal selenium single crystals which are parallel (curve 1) and perpendicular (curve 2) to “c” axis.

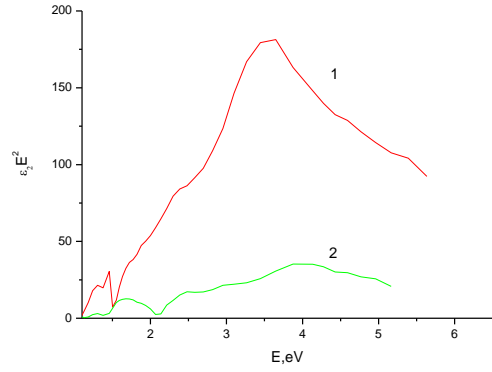


Fig.5. The spectra of $\epsilon_2 E^2$ integral function of bound state density of hexagonal selenium single crystals which are parallel (curve 1) and perpendicular (curve 2) to “c” axis.

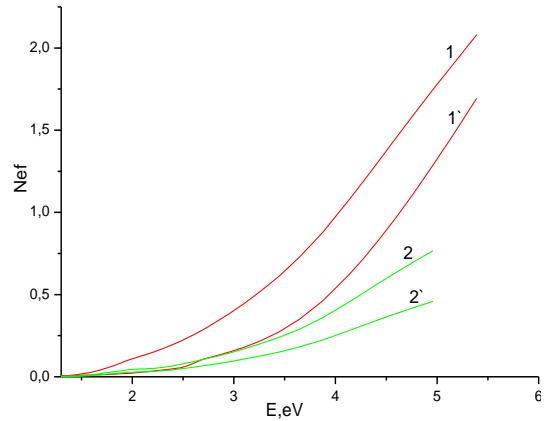


Fig.6. The spectra of effective number of valent electrons $N_{ef}(E)$ $-Img\epsilon^{-1}(E)$ and $-Img(\epsilon+1)^{-1}(E)$ of hexagonal selenium single crystals which are parallel (curve 1) and perpendicular (curve 2) to “c” axis.

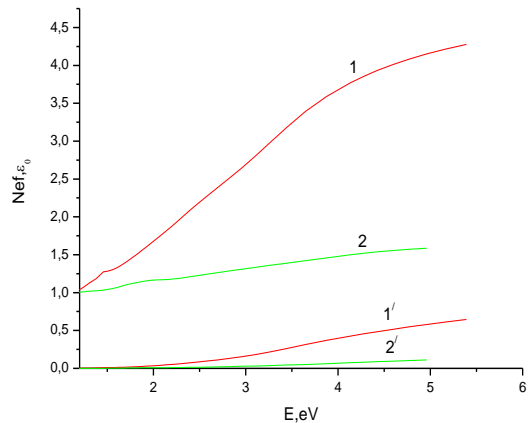


Fig.7. The spectra of $\epsilon_{0,eff}(E)$ effective static dielectric constant and effective number of valent electrons $N_{ef}(E)$ taking part in transitions up to the given energy E of hexagonal selenium single crystals which are parallel (curve 1,1') and perpendicular (curve 2,2') to “c” axis.

As it is mentioned in [48], the study of absorption transitions on materials is impossible because of big

absorption value in region of energy interband transitions $E > E_g$ (E_g is minimal energy of interband transitions called forbidden band energy). The reflection stays the unique effective method. On the other hand, the analytical singularities of imaginary parts of complex dielectric constant $\varepsilon_2(E)$ and functions bound by state densities dN/dE almost coincide. The gradient $\nabla_k E_{ij}$ of band-to-band distance makes the main contribution in analytical singularity of dN/dE function.

$$\frac{dN_{ij}}{dE} \sim \int \frac{dS_k}{|\nabla_k E_{ij}|},$$

where $E_{ij}(k) = E_j(k) - E_i(k)$ is distance between conduction and valence bands. The values dN/dE near critical points in k -space confirmed by $|\nabla_k E_{ij}| = 0$ expression and also the displacement of critical points and transition type. The analysis of $\varepsilon_2(E)$, dN/dE function and $R(E)$ reflection coefficient show that the disposition in energy spectrum and peak character are similar ones or they are very close to these parameters. That's why one can define the values of corresponding interrecord gaps and nature bands with the help of direct coincidence of experimental data on curves and crystal reflection in $E > E_g$ region with theoretical calculations of dN/dE function.

It is known that the least E_g energy between occupied and free states is the one of the very important semiconductor parameters. The high transparency in wide energy region $E < E_g$ is character for non-crystalline materials. The several methods of its definition and evaluations by the level of $\alpha(E)$ absorption coefficient of long-wave absorption edge are known. The exact value of E_g for non-crystalline semiconductors is discussion one and usually, the discussion of $\alpha(E)$ spectrum character in Urbach and Tauc models is carried out without evaluations E_g [49]. E_g is defined by the value of absorption coefficient $\alpha(E) = 10^3 \text{cm}^{-1}$ from Tauc model.

As it is mentioned in [49] $N(E)$ density of states is the perception which similarly suitable for both crystalline and non-crystalline substances. By existing results of experimental data the motion of density of states in non-crystalline substance doesn't strongly differ from corresponding one in crystal. The thin structure in first case can be lubricated and the local states can appear in forbidden band, the band structure is kept, i.e. it is defined by atom short-range order in materials.

As it is mentioned in [50] one can't carry out the principal boundary between single monocrystalline, polycrystalline and amorphous substance state. The presence of band structure which is forbidden band and conduction band can be taken from the fact of atom short-range order and for this conclusion there is no need to require the atom periodic disposition. These questions for

amorphous and crystalline selenium have been studied in [1,2,51-53], are defined and their electron structures are compared. As it is mentioned in [31] the general scheme of energy bands is mainly defined by crystal structure and material external configuration, but not atoms.

The selenium crystallizes into crystal structure of special type consisting of spiral chains with three atoms in elementary cell. The selenium structure can be also considered as one consisting of three coherent simple hexagonal lattices each of which gives by one atom in elementary cell. The spiral chain radius for selenium is equal 1,07Å, the angles between Se-Se-Se atoms in chain are approximately equal to 105° , the distance between neighbor selenium atoms in the chain is 2.32Å, the relation of distances between the neighbor atoms belonging to different chains and one and the same chain is equal to 1,49. That's why it is expected that interaction between atoms in limits of the given chain will be stronger than the one between different chains. Buy this reason, the some selenium main properties can be explained considering the only the separate chain. The analysis of selenium structure symmetry is given by Azendorf [54]. The selenium structure has D_3 group symmetry. The space group isn't symmorphic one and some operations of symmetry are connected with fractional translations. The selenium space group has the screw axes of third order.

The selenium presents itself the elements of sixth group of periodic system, electron configuration of its free electrons (ns^2), $n=4$.

The internal membranes are totally occupied; the main states with approximately same energies than atoms have correspond them in crystal.

The band structures of selenium and tellurium in one-dimensional approximation are studied by several authors. The early simplest explanation belongs to Reitzu [55], the more detail calculation had been carried out by Olekhno and Nox [56] (in limits of the method of strongly bound electrons with the use of semiempirical screening of exchange potential).

In three-dimensional case the calculation is carried out by Treish and Sandrok [57] (by Green function method).

In selenium the bottom of the conduction band and the top of valent band are in H point taking under the consideration the correspondence between crystalline and atomic wave functions of electrons. It is considered that valent and conduction bands form from p -levels and they can be divided on three regions between which the forbidden energy regions are. It is necessary to note that elements of sixth group of periodic system present all types of electron structures: oxygen and sulphur are isolators, tellurium and selenium are semiconductors, and polonium is the metal.

Table.

Sample	Optical transitions defined by maximums $\varepsilon_2(E)$ in interval of photon energy 1÷6 eV								
Parallel to «c» axis	1,55	1,65	1,87	2,37	3,43	3,63	-	-	-
Perpendicular to «c» axis	1,54	1,68	1,87	2,38	2,48	2,94	3,87	4,13	4,59

Thus, the spectra of their all optical parameters in energy interval 1-6eV both perpendicular and parallel to "c" axis are defined, the interband optical transitions that gives the possibility to clear their band structures are

defined in the given paper on the base of measurement of light reflection in hexagonal selenium single crystals grown up under the pressure 4,5 kbar.

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