

Experimental and theoretical studies of orientational dependence of x-ray reflectivity in vicinity of S K-edge in hexagonal CdS crystal

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2004 J. Phys.: Condens. Matter 16 4597

(<http://iopscience.iop.org/0953-8984/16/25/017>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 27/05/2010 at 15:38

Please note that [terms and conditions apply](#).

Experimental and theoretical studies of orientational dependence of x-ray reflectivity in vicinity of S K-edge in hexagonal CdS crystal

E O Filatova^{1,2}, J-M André^{2,3}, E Yu Taracheva¹, A J Tvaladze⁴,
V L Kraizman⁴, A A Novakovich⁴ and R V Vedrinskii⁴

¹ Institute of Physics, St-Petersburg University, St-Petersburg, 198904, Russia

² Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, Université Paris Sud, 7614 Orsay, France

³ Laboratoire de Chimie Physique, Université Pierre et Marie Curie, 7523 Paris, France

⁴ Rostov State University, Rostov on Don, 344006, Russia

Received 13 September 2003

Published 11 June 2004

Online at stacks.iop.org/JPhysCM/16/4597

doi:10.1088/0953-8984/16/25/017

Abstract

The reflection spectra of a hexagonal CdS crystal in the region of S K-absorption edge were studied both experimentally and theoretically. It was found that the reflection spectrum fine structure as well as the absolute value of reflectivity of the crystal surface cut parallel to the crystal optical axis depends on the surface orientation with respect to the polarization of incoming radiation.

1. Introduction

CdS is a technologically important material. For many years it has been used in electric device applications. At present it is one of the main materials for nanoelectronics [1–4].

CdS crystal exists in two modifications: zincblende and wurtzite. Many efforts have been invested in the study of the electronic structure of both modifications and their optical properties in the ultraviolet region (1.2–12 eV) [5–12]. The bulk of the experimental information comes from reflectivity measurements employing polarized radiation or light of mixed polarization. In the x-ray region most of the data are concerned with cubic CdS investigations. Absorption measurements near the S $L_{2,3}$ -absorption edge were performed for evaporated films and for a thin film of single crystal [13–20]. The $L_{2,3}$ -emission spectrum has been obtained in [13, 21]. There are only very few data obtained near the S K-absorption edge, especially in hex.CdS crystal (wurtzite modification). At the same time the character of the crystalline structure of hex.CdS leads to the anisotropy of the interaction with polarized radiation. According to [22], so-called linear dichroism caused by the angular dependence of dipolar absorption exists in hex.CdS. It should be noted that up to now there has been no experimental confirmation of the existence of linear dichroism near the S K-edge in hex.CdS. The calculations presented in the work [23] strongly support this phenomenon in hex.CdS.

In this paper the experimental investigation of reflection spectra near the sulfur K-edge in hexagonal CdS is presented. The spectra were measured for two different crystal orientations with respect to the electric field vector with the help of s-polarized radiation. To find out the origin of the discovered orientation dependence of the measured reflection spectra a theoretical investigation has been carried out.

2. Cadmium sulfide crystals

As it has been said above, CdS crystal exists in two modifications: zincblende and wurtzite. The chemical bonding of both phases is commonly described by sp^3 hybridization. In both structures, the coordination shell of the anion is made up of four cations in tetrahedral symmetry and the second neighbouring shell is made up of 12 anions. One can look on these structures as having closely packed ions of S with Cd ions in tetrahedral voids. Although these structures show large similarities they also reveal a number of distinctions. For zincblende the cubic packing is characteristic, which means that closely packed layers are perpendicular to the four polar directions $\langle 111 \rangle$. By contrast, the hexagonal packing corresponds to the wurtzite phase. In this case the only polar direction $[0001]$ exists with closely packed layers perpendicular to it. Another peculiarity of wurtzite is the position of the foot of the tetrahedron in the layers. The triangular feet of the tetrahedrons in every following layer must be rotated by 60° . Each vertex is shared by four tetrahedrons.

Hex.CdS crystal belongs to the $C_{6v}(6mm)$ local point group in contrast with cub.CdS (zincblende modification), which falls in the $T_d(\bar{4}3m)$ local point group. Wurtzite is a uniaxial crystal with optical axis parallel to the crystallographic axis c .

Traditionally the hexagonal prism is used as the simplest structure to describe the hexagonal modification. The projection of the wurtzite structure on a base plane (0001) is plotted in figure 1. As may be seen from the figure, the wurtzite structure consists of binary layers, each determined by two sublayers of ions of different sort. Three bonds exist for each ion within a basal plane of the binary layer and one bond for each ion between binary layers. The binary layers are parallel to the base plane (0001) .

3. Experimental and sample details

The angular and spectral dependences of the reflectivity near the S K-absorption edge were carried out in a reflectometer set-up on the SB3 synchrotron beam line 'MOGOTOX' (monochromator and goniometer for x-ray optics treatment) [24] of the Super ACO storage ring of LURE at Orsay. Si crystal sheets with reflectivity above 50% were used in the experiment. The energy resolution near the S K-edge was better than 1 eV. The $\theta-2\theta$ goniometer has several degrees of freedom, which permits the sample to move into and out of the incident beam. The detector was a gas flow proportional counter closed with a system provided with a polypropylene window supported by a metallic grid. It works with a 90%/10% argon/methane mixture. High spectral purity was achieved by means of the detector being used in the proportionality mode with a single channel analyser. The radiation impinging on the sample mirror was s-polarized.

A surface cut parallel to the crystallographic c -axis of a single crystal hex.CdS and variously oriented with respect to the electric field vector was investigated (crystal orientations B_1 and B_2 ; see figure 2). Since the same part of the sample surface was studied in the both cases, the value of the rms-roughness was also the same. Nevertheless, planar anisotropy is possible, for example due to different roughness correlation lengths for different directions. Indeed, a strong effect of planar anisotropy was detected in a hex.BN crystal [25].

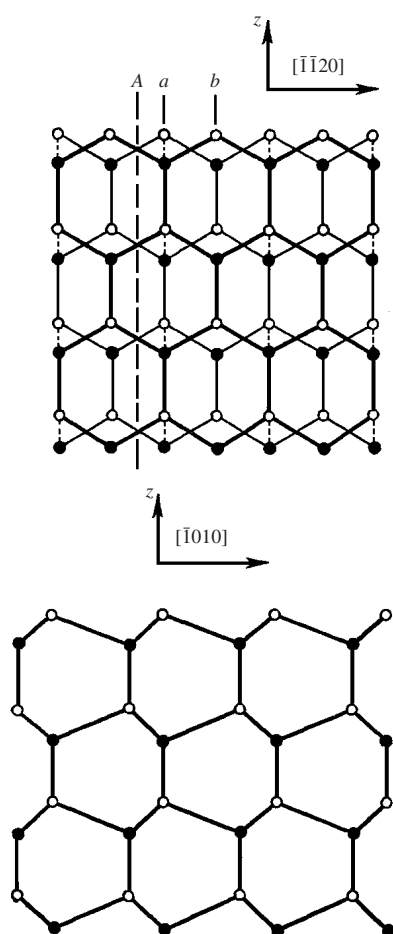


Figure 1. The projection of the wurtzite structure on a base plane (0001) [28].

4. Results and discussion

Figure 3 shows the reflection spectra of the hex. CdS crystal obtained near the S K-absorption edge for grazing incidence angles $\theta = 0.6^\circ$, 0.8° , and 1° for the crystal orientations B_1 and B_2 (see figure 2).

One can see that both the reflection spectra fine structure and the overall reflectivity depend on crystal orientation.

Analysis of the reflection spectra fine structure indicates that the reflection spectra for both orientations and all angles have the same number of principal features of the reflection spectra fine structure, and the energy positions of these features are independent on the crystal orientation at all investigated angles. In contrast, the intensity and the shape of some peaks depend on crystal orientation. For the smallest incidence angle $\theta = 0.6^\circ$ the shape of the reflection spectra depends on the crystal orientation only slightly. The growth of the incidence angle leads to the orientational dependence of the feature M centred at above 2480 eV. Its shape slightly depends on the incidence angle in the case of crystal orientation B_2 , whereas for the orientation B_1 there appears a narrow feature M' , the intensity of which increases with the growth of the angle. The character of the orientation dependence of the S K-reflection spectra

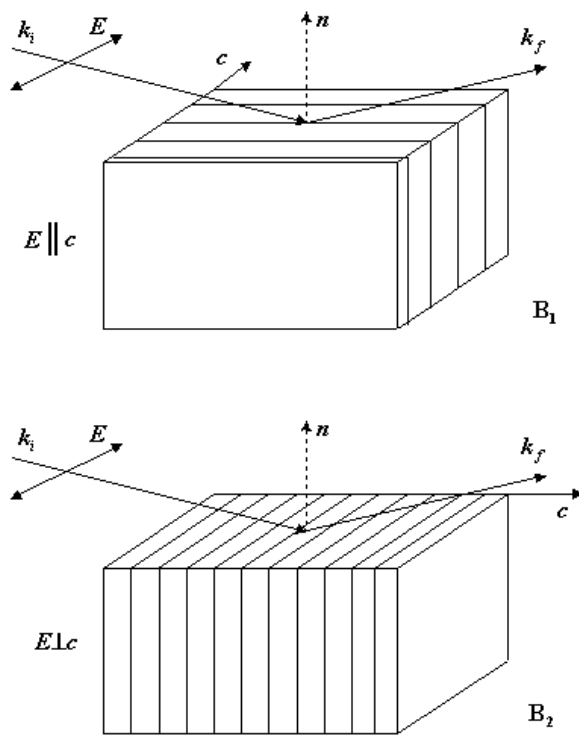


Figure 2. Different orientations of the hex.CdS crystal with respect to the electric field vector E . B_1 and B_2 label the crystal orientation.

as deduced from experiments is in a good agreement with the dependences obtained in the ultraviolet region [12] and near the S $L_{2,3}$ -edge [16].

According to figure 3, the absolute values of the reflectivity differ significantly for two orientations of the same crystal surface at small incidence angles though the S K-reflection spectra have similar fine structures. The angular dependences of the reflectivity $R(\theta)$ at different energies that belong to the region of normal dispersion as well as to the anomalous region were measured. The reflectivity for orientation B_1 is greater than for orientation B_2 at all investigated energies in the range of small incidence angles. For example, figure 4 shows the angular dependences of the reflectivity for crystal orientations B_1 and B_2 obtained at energy $E = 3200$ eV (range of normal dispersion). As one can see, the reflectivity for the face B_1 is larger than that for the face B_2 in the region of normal dispersion too.

In the strict sense the permittivity within any actual sample depends on the distance from the sample surface as well as on in-surface plane coordinates. The transitional layer with disordered structure exists in any actual sample near the surface. There are a lot of reasons for the existence of such layers, and one of them is a technological treatment of the surface. The technological treatment of the sample surface produces a mechanically destroyed surface layer. Such a disordered layer in the analysed surface obviously affects the process of reflection, making it similar to that from a polycrystalline sample, and therefore weakening the effect of the sample orientation. An increase in the grazing incidence angle leads to a greater probing depth and hence to the participation of more perfect layers in forming the reflected beam. Concerning the surface roughness, it should be noted that the same but differently orientated surface was investigated in both cases. So it would be natural to assume that the discovered difference in absolute value of reflectivity is caused by the planar anisotropy of the surface. The angular dependence of the absolute value of the reflection coefficients for two crystal surface

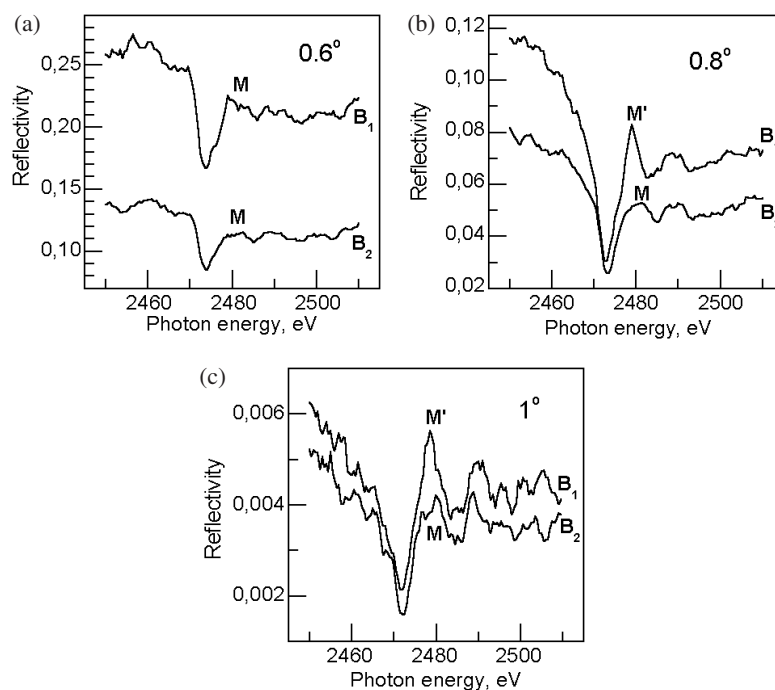


Figure 3. The reflection spectra of the hex. CdS crystal obtained near the S K-absorption edge for different grazing incidence angles θ with the help of s-polarized radiation for crystal orientations B_1 and B_2 . (a) $\theta = 0.6^\circ$, (b) 0.8° , (c) 1° .

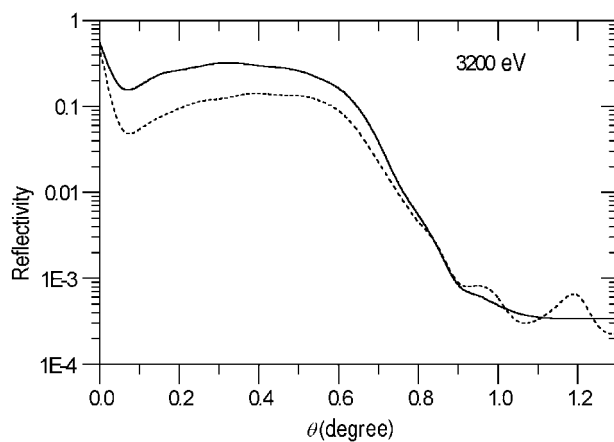


Figure 4. Angular dependences of the reflection coefficient obtained for crystal orientations B_1 and B_2 for energy 3200 eV with the help of s-polarized radiation. The solid curve denotes the data for the orientation B_1 and the dotted curve denotes the data for orientation B_2 .

orientations is noteworthy. According to theoretical predictions the influence of the surface roughness on the reflectivity increases with the growth of the incidence angle [26, 27]. By contrast, the discrepancy between the reflectivity for crystal orientations B_1 and B_2 decreases with the growth of the incidence angle. According to [27] the growth of the incidence angle leads to the redistribution of the intensities of the specula and the diffused scattered intensities.

The majority of the diffused scattered intensity falls into the specula component and cannot be recorded in the experiment. The contribution of the scattered intensity rises with the increase of the incidence angle.

It should be emphasized that it is a huge problem to take into account the surface roughness in the case of uniaxial crystals. The problem connects with the existence of composite microstructure on the surface of anisotropic crystals. The surface of any crystal side of uniaxial crystals especially cut parallel to the crystallographic axis will be disrupted by splits after any type of technological polishing. So a prerequisite to the formation of a scattering into the substance, in addition to scattering into vacuum, is produced. Up to now no theoretical description of the scattering deep into the material has been available.

To find out the origin of the discovered orientation dependence of the measured S K-reflection, a spectrum fine structure theoretical investigation has been carried out.

5. Calculations

The permittivity of a crystal is practically isotropic when the x-ray photon energy is far from the absorption edges of the atoms in the crystal. In contrast, in near-edge ranges the permittivity tensor of a crystal may be noticeably anisotropic. This anisotropy leads to such well-known crystal optics phenomena as pleochroism, birefringence, etc.

The permittivity tensor of the crystal ε_{ij} is expressed through the atomic forward scattering factor (AFSF) by the relation [29]

$$\varepsilon_{ij}(\omega) = \delta_{ij} - 4\pi \sum_k n_k \frac{c^2 r_0}{\omega^2} f_{ij}^{(k)}, \quad (1)$$

where $f_{ij}^{(k)}$ is the AFSF of the k th atom in the cell, n_k is the concentration of such atoms in the crystal, ω is the x-ray wave frequency, c is the light velocity, and r_0 is the classical electron radius.

It was shown in [30, 31] that in the vicinity of atomic core-level edges the AFSF of an atom in the crystal can be represented as a sum of two terms, where the first is the AFSF of the isolated atom and the second is a correction caused by the scattering of slow virtual photoelectrons from the atoms surrounding the one scattering x-rays:

$$f_{ij} = f_0 \delta_{ij} + \Delta f_{ij}. \quad (2)$$

The first term is isotropic and can be found either in tables [29] or is available in [32]. This term contains normal and anomalous contributions into the AFSF for the isolated atom. The second term, which we will name hereafter the virtual electron scattering correction (VESC), is non-negligible only near the absorption edges, or, in other words, in the anomalous scattering range. This term is responsible for the x-ray dichroism.

The VESC term is calculated by the multiple scattering method in a Green function formalism described in detail in [29]. This method gave good results earlier for calculations of XANES and reflectivity fine structure [33–35].

Calculations of the VESC to the AFSF of the sulfur atom in the crystal have been performed in two stages. First, we calculated the S K-absorption spectrum and determined the Fermi energy and then the VESC itself was calculated.

In order to clarify the nature of the observed dichroism, the dependence of the absorption spectrum on the cluster size was studied. The spectra for two clusters were calculated. The first one contains 17 atoms and is made up of four CdS_4 tetrahedrons, which share the central absorbing sulfur atom. Ninety-eight atoms disposed in the sphere with radius 8.3 Å centred at the absorbing S atom made up the second cluster. Crystal structure data were taken from [36]. The method of cluster potential construction is described in [34, 35].

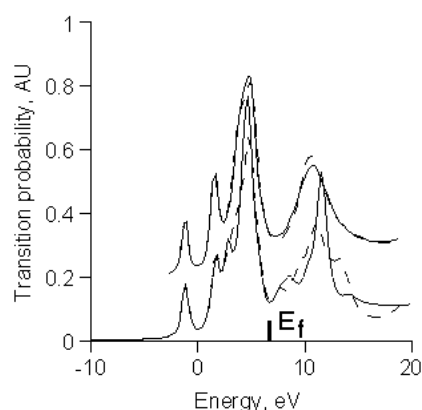


Figure 5. The S K-electron transition probability to the continuum p-states of the hex.CdS crystal calculated for the 17-atom cluster (upper curves, shifted upwards for clearance) and for the 98-atom cluster (lower curves). The x-ray wave is s-polarized: $E \parallel c$ —solid curves; $E \perp c$ —dashed curves.

Spectra calculated for two orientations of the electric field vector E of s-polarized incoming radiation either parallel or perpendicular to the optical c -axis of the crystal are shown in figure 5. One can see that in the case of the 17-atom cluster the spectra for the two polarizations practically coincide with each other, whereas in the case of the 98-atom cluster a noticeable difference is observed between them. Therefore one can conclude that the dichroism in hex.CdS crystal is caused by photoelectrons scattered from the atoms disposed in distant coordination shells. This is not in contradiction with the conclusion made in [23]. According to [23], the dichroism in the hex.CdS crystal is caused by photoelectron scattering from atoms of more distant shells.

It is worth noting that one-electron calculation methods give the features in the spectrum caused by the electron transitions to both vacant and occupied states in the crystal. So we have to understand where the Fermi level is placed and exclude the features in the theoretical spectra which are caused by the electron transitions to the occupied states. In the case of dielectrics with a wide gap this is easy to do. Cadmium sulfide is a semiconductor crystal, therefore one cannot expect a pronounced gap in the K-spectra. Comparing the results presented in figure 5 with the calculated K-absorption spectrum of an isolated S atom, one can conclude that the structure at energy below 7 eV is caused by electron transitions from the 1s shell to the valence band constructed mainly from S 3p states. A dip at about 7 eV, which is present in all curves in figure 5 and also in the Cd K-spectrum, corresponds to the forbidden gap. We therefore accept a value 7 eV for the Fermi energy and employ it hereafter for AFSF calculations.

The real and imaginary parts of anomalous contributions to the sulfur AFSF tensor components Δf_{\perp} and Δf_{\parallel} calculated in the 98-atom cluster are depicted in figure 6. Both real and imaginary parts of these components differ from each other in the anomalous scattering range and practically coincide outside it.

Employing the AFSF term f_0 for S and Cd atoms from [32], the permittivity tensor components were calculated according to formulae (1, 2). In the case of a uniaxial crystal, the permittivity tensor is diagonal if one of the coordinate axes is directed along the optical axis of the crystal. This allows us to obtain a simple generalization of Fresnel's formulae for s-polarized radiation [33] for the reflectivity $R_s(B_i)$ for B_i crystal orientations (see figure 2).

$$\begin{aligned}
 R_s(B_1) &= \left| \frac{\sin \theta - \sqrt{\varepsilon_{\parallel} - \cos^2 \theta}}{\sin \theta + \sqrt{\varepsilon_{\parallel} - \cos^2 \theta}} \right|^2 \\
 R_s(B_2) &= \left| \frac{\sin \theta - \sqrt{\varepsilon_{\perp} - \cos^2 \theta}}{\sin \theta + \sqrt{\varepsilon_{\perp} - \cos^2 \theta}} \right|^2.
 \end{aligned} \tag{3}$$

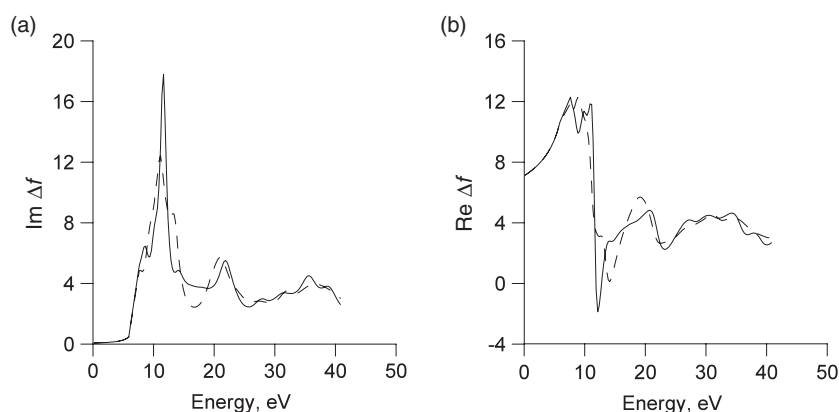


Figure 6. Imaginary (a) and real (b) parts of anomalous scattering corrections to the sulfur AFSA in hex.CdS crystal calculated for the 98-atom cluster. Δf_{\perp} —solid curve, Δf_{\parallel} —dashed curve.

As was mentioned above, the experimental reflection spectra as well as the absolute value of reflectivity depend on the orientation of the crystal surface with respect to the incident beam. It is a clear indication that this surface is not isotropic from both the microscopic and macroscopic points of view. As far as we know a rigorous theory of surface roughness influence on x-ray reflectivity has not yet been developed for the anisotropic case.

To take into account the surface roughness influence on the intensity of a beam reflected from an isotropic surface, several approaches have been developed [37]. At small grazing incidence angles θ ($\pi a\theta^2/\lambda \ll 1$) the approximate formula

$$R = R_F \exp \left[- \left(\frac{2\pi}{\lambda} \right)^{3/2} \frac{\sigma^2}{\sqrt{a}} \theta \right] \quad (4)$$

has been proposed [37], where R_F is the reflectivity calculated by Fresnel's formula, σ is the rms roughness height, and a is the radius of the roughness height correlation.

At large θ angles ($\pi a\theta^2/\lambda \gg 1$) one has to use another expression:

$$R = R_F \exp \left[- \left(\frac{4\pi}{\lambda} \sigma \sin \theta \right)^2 \right]. \quad (5)$$

In the case studied, formula (4) is applicable to the spectrum measured at 0.6° and at a stretch to that measured at 0.8° , whereas the attenuation of the spectrum at 1° is described better by expression (5). Moreover, both formulae are applicable rather to the smooth isotropic surfaces of deposited films than to uniaxial crystal surfaces after treatment. (See the discussion at the end of section 4.) Indeed, we have failed to find the value of the fraction σ^2/\sqrt{a} or σ^2 providing the correct relation R_F/R for all three angles for certain crystal orientations.

At the same time, within the short energy interval in which the reflection spectrum fine structure is studied in the present paper, the exponential factors in both formulae practically do not depend on energy. Hence to compare the fine structure of theoretical spectra with experimental ones we suppose that the roughness influence can be approximately taken into account just by the multiplication of Fresnel's reflectivity by a factor depending only on grazing incidence angles and crystal surface orientation.

A comparison of calculated reflection spectra with experimental ones is shown in figure 7. One can see that after multiplication of the calculated spectra by appropriate factors caused by the roughness influence the theoretical reflectivity fine structures are in good agreement with

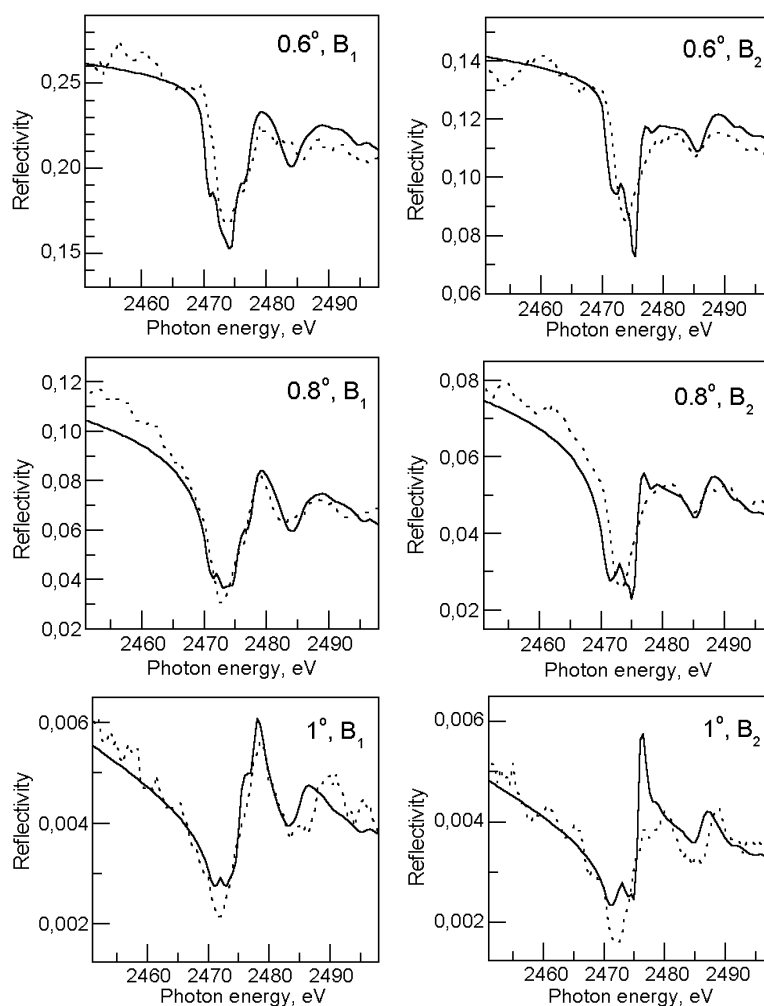


Figure 7. Comparison of calculated reflection spectra from a hex.CdS crystal near the S K-edge with experimental data. Spectra calculated in Fresnel's approach are multiplied by appropriate factors to take into account the surface roughness influence. Grazing incidence angles and crystal orientations are depicted near the curves. The solid curve denotes the calculated reflection spectra and the dotted curve denotes the experimental data.

experimental data for all angles and surface orientations. The spectra for grazing incidence angle $\theta = 1^\circ$ are noteworthy. One can see that a very narrow peak and a shoulder describe the main near edge feature in the calculated reflection spectrum for the B_2 crystal orientation whereas the same structure in the experimental spectrum has a plane top. Probably this disagreement is caused by insufficient energy resolution in the experiment.

6. Conclusions

The experimental and theoretical studies of the near edge reflection spectra fine structure in the region of the S K-absorption edge for a hex.CdS single crystal are presented. It is established that the fine structure of the reflection spectra as well as the absolute value of the reflectivity depend on the orientation of the crystal surface cut parallel to the optical axis with respect to the

s-polarized incident beam. Calculations performed strongly suggest that the reflectivity fine structure variation in a uniaxial hex.CdS crystal is caused by virtual photoelectron scattering from the atoms disposed in distant coordination shells. The difference in reflectivity is caused by planar anisotropy of the crystal surface. Measurements under conditions of better energy resolution as well as further theoretical investigations are indispensable for a more detailed comprehension of the dichroism in hex.CdS.

Acknowledgments

The authors wish to thank M Briat, C Rémond and R Marmoret at the Commissariat à l'Energie Atomique for help in measurements. The authors are grateful to Professor O F Vivenko for the supply of the samples used in this study.

References

- [1] Liu S-M, Guo H-Q, Zhang Z-H, Li R, Chen W and Wang Z-G 2000 *Physica E* **8** 174
- [2] Zuhr R A *et al* 1999 *Nucl. Instrum. Methods Phys. Res. B* **148** 991
- [3] Bhattacharjee B, Ganguli D and Chaudhuri S 2002 *J. Fluorescence* **12** 369
- [4] Mostafavi M, Liu Y-P, Pernot P and Belloni J 2000 *Radiat. Phys. Chem.* **59** 49
- [5] Ninomiya S and Adachi S 1995 *J. Appl. Phys.* **78** 1183
- [6] Cardona M and Harbeke G 1965 *Phys. Rev.* **137** A1467
- [7] Cardona M 1963 *Solid State Commun.* **1** 109
- [8] Cardona M 1963 *Phys. Rev.* **129** 1068
- [9] Cardona M, Weinstein M and Wolf G A 1965 *Phys. Rev.* **140** A633
- [10] Walker W C and Osantowski J 1964 *J. Phys. Chem. Solids* **25** 778
- [11] Kindig N B and Spicer W E 1965 *Phys. Rev.* **138** A561
- [12] Bergstresser T K and Cohen M L 1967 *Phys. Rev.* **164** 1069
- [13] Eichhoff G 1958 *Ann. Phys.* **1** 55
- [14] Cardona M and Haessel R 1963 *DESY Preprint* 69/45
- [15] Sugiura C, Hayashi Y, Konuma H, Sato S and Watanabe M 1970 *J. Phys. Soc. Japan* **29** 1645
- [16] Watanabe M, Yamashita H, Nakai Y, Sato S and Onari S 1971 *Phys. Status Solidi b* **43** 631
- [17] Sugiura C, Hayashi Y, Konuma H and Kiyono S 1971 *J. Phys. Soc. Japan* **31** 1784
- [18] Euwema R N, Collins T C, Shankland D G and Dewitt J S 1967 *Phys. Rev.* **162** 710
- [19] Li D, Bancroft G M, Kasrai M, Fleet M E, Feng X H, Tan K H and Yang B X 1994 *J. Phys. Chem. Solids* **55** 535
- [20] Gilbert B, Frazer B H, Zhang H, Huang F, Banfield J F, Haskel D, Lang J C, Srajer G and De Stasio G 2002 *Phys. Rev. B* **66** 245205
- [21] Meisel A and Szargan R 1968 *The Int. Symp. on X-ray Spectra and Electronic Structure of the Substance (Kiev, 1968)* vol 1, p 297
- [22] Brouder C 1990 *J. Phys.: Condens. Matter* **2** 701
- [23] Levelut C, Sainctavit Ph, Ramos A and Petiau J 1995 *J. Phys.: Condens. Matter* **7** 2353
- [24] Filatova E O, Lukyanov V A, Barchewitz R, André J-M, Idir M and Stemmler P I 1999 *J. Phys.: Condens. Matter* **11** 3355
- [25] Filatova E O and Lukyanov V A 2002 *J. Phys.: Condens. Matter* **14** 11643
- [26] Kozhevnikov I V *et al* 1995 *Proc. SPIE* **2453** 47
- [27] Asadchikov V E *et al* 1998 *Surface (Russia)* **7** 17
- [28] Shaskolskaya M G 1976 *Crystallography (Russia)* 390
- [29] Henke B L, Lee P, Tanaka T J, Shimabukuro R I and Fujikawa B K 1982 *At. Data Nucl. Data Tables* **27** 1
- [30] Vedrinskii R V, Kraizman V L, Novakovich A A and Machavariani V Sh 1992 *J. Phys.: Condens. Matter* **4** 6155
- [31] Ankudunov A L and Rehr J J 2000 *Phys. Rev. B* **62** 2437
- [32] <http://physics.nist.gov/PhysRefData>
- [33] Vedrinskii R V, Kraizman V L, Novakovich A A and Machavariani V Sh 1993 *J. Phys.: Condens. Matter* **5** 8643
- [34] Poumellec B, Kraizman V, Aifa Y, Cortès R, Novakovich A and Vedrinskii R 1998 *Phys. Rev. B* **58** 6133
- [35] Vedrinskii R V, Kraizman V L, Novakovich A A, Elyafi Sh M, Bocharov S, Kirchner Th and Dräger G 2001 *Phys. Status Solidi b* **226** 203
- [36] <http://Database.iem.ac.ru/mincryst>
- [37] Vinogradov A V (ed) 1989 *Zerkal'naya Rentgenovskaya Optika* (Leningrad: Mashinostroyeniye)