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Dispersion of Optical Constants in CdP₂

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Spectral dependences of the gyration tensor components g_{11}, g_{33}, refraction indices and birefringence of tetragonal CdP₂ are investigated at 300 K. The optical activity of the crystal is found to be determined by both the crystal and the molecular contributions, the latter being due to the distortion of the tetrahedral symmetry of the structural elements. The dispersion of the refractive indices is discussed on the basis of a single-effective-oscillator model. The ionicity of CdP₂ is equal to 0.56 and is close to the values of $A^{II}B^{VI}$ compounds and the ionicity of Cd–P bond in $A^{II}B^{IV}C_2^V$ semiconductors. The dispersion of the spectroscopic properties of CdP₂ is concluded to be mainly determined by the Cd–P bound.

Исследуется спектральная зависимость компонент гирационного тензора g_{11}, g_{33}, показателей преломления и двупреломления тетрагонального CdP₂ при 300 К. Установлено, что оптическая активность кристалла определяется как кристаллическим, так и молекулярным вкладом, при этом последний обусловлен искажением характерных структурных тетраэдров. Дисперсия показателей преломления исследуется на основе модели единичного-эффективного осциллятора. Получено, что ионность CdP₂ равняется 0,56 и по своему значению близка к ионностям соединений типа $A^{II}B^{VI}$, а также связей Cd–P в полупроводниках $A^{II}B^{IV}C_2^V$. Заключается, что дисперсия спектроскопических свойств CdP₂ в основном определена связью Cd–P.

1. Introduction

The crystals of β-CdP₂ belong to the tetragonal system (space group D_4^4 or D_4^8) [1]. Though the structure of the compound has no pronounced anisotropic features [2], CdP₂ appears to be greatly birefringent and exhibits considerable rotatory power along the optical axis [3]. Therefore, an interest in the magnitude and spectral dependence of the optical activity effects in other, more general crystallographic directions arises. It should be noted that the study of the dispersion of optical constants is useful in ascertaining the origin of the optical properties and, on the other hand, allows one to determine the ionicity of crystals in the frame of various models. The latter quantity has proved to be important in ordering a number of properties of semiconductors [4].

In this work the optical activity of CdP₂ has been studied along the optical axis of the crystal as well as in the perpendicular direction. Corresponding gyration tensor components have been determined. The origin of optical activity in CdP₂ is discussed. Dispersions of the optical activity parameters, refractive indices, and birefringence are examined on the basis of single-effective-oscillator models. The ionicity of the compound is analyzed according to the dielectric theory of chemical bonding.

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2. Experimental

Measurements were carried out on tetragonal CdP_2 single crystals grown from the vapour phase. Samples oriented by X-ray diffraction were prepared in the form of plane-parallel plates with thickness d in the range 25 to 200 μm. The spectra were measured at 300 K using a SPM-2 monochromator, Glan prisms, and a conventional phase-sensitive detection technique.

According to the symmetry of CdP_2 crystals, the gyration tensor g_{ij} has two non-zero components g_{11} and g_{33} [5]. The values of g_{33} were determined from the measurements of the rotation angle ψ of the plane-polarized light propagating along the optical axis using the relation $\psi = \pi g_{33}/n_0\lambda d$, where n_0 is the ordinary refractive index. The measured values of the rotatory power $\varrho = \psi/d$ along the optical axis agree well with those obtained in [3].

The gyration tensor component g_{11} cannot be found in such a straightforward manner because of the linear birefringence. It may be determined by studying the state of light polarization in the crystal. Let a linearly polarized light strike a crystal plate, its direction being normal and its polarization parallel to the optical axis c. Then the transmission of the sample for the crossed analyzer is expressed by the following equation [6]:

$$\Gamma = \frac{\left(\dfrac{G}{\bar{n}}\right)^2}{(n' - n'')^2 + \left(\dfrac{G}{\bar{n}}\right)^2} \sin^2\left\{\left(\frac{\pi d}{\lambda}\right)\left[(n' - n'')^2 + \left(\frac{G}{\bar{n}}\right)^2\right]^{1/2}\right\}, \tag{1}$$

where $G = g_{ij}l_il_j$ is the gyration [5] (l_i, l_j are the direction cosines), n', n'' are main refractive indices when gyration is neglected, and $\bar{n} = \sqrt{n'n''}$. Equation (1) shows that in this case transmission spectrum is a fringe curve. From its parameters the absolute values of G and linear birefringence $\Delta n = n' - n'' \approx n_e - n_0$ were determined.

The spectra of n_0 and Δn were also measured by the interference method. The extraordinary refractive index n_e was calculated from the experimental data of n_0 and Δn. The obtained values of refractive indices and birefringence are in agreement with those determined in [3] by the prism method.

3. Results

The spectra of the gyration tensor components g_{11} and g_{33} are shown in Fig. 1. It is seen that the dispersion of g_{33} is more pronounced than that of g_{11}, and $|g_{33}| < |g_{11}|$ in all the investigated spectral range. The corresponding specific rotativity along the optical axis defined as [7]

$$\xi = -\frac{\lambda^2\varrho}{2\pi^2(n^2 - 1)^2} \tag{2}$$

and is approximately constant in the transparent region. For CdP_2 the value of $|\xi| = 1.4 \times 10^{-10}$ cm is somewhat higher than that of ZnP_2 (1.1×10^{-10} cm) [8], but is close to the average value for the optically active crystals [7].

The spectra of g_{11} and g_{33} can be well described by both the Chandrasekhar and the Drude models [9]. Fitting Drude's formula to the experimental data of g_{33}, the characteristic energy (2.46 eV) is close to the position (2.39 eV [10]) of the first CdP_2 reflection peak pronounced for $e \perp c$ polarization. The same characteristic energy value follows from the corresponding spectrum of circular birefringence $\delta n = \varrho\lambda/\pi$ [5]
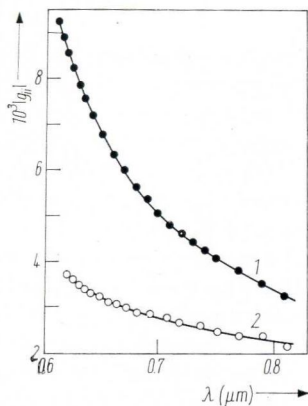
Fig. 1. Experimental (points) and calculated (solid lines) spectra of gyration tensor components g_{33} (1) and g_{11} (2)

(Fig. 2). Taking into account the Kramers-Kronig relations, the reflectance peak at 2.39 eV is expected to be highly circularly dichroic.

The oscillator energy (3.38 eV) obtained from the dispersion of g_{11} does not correspond to any particular peak in the reflectance spectra and therefore it is the average for many interband transitions.

The spectral dependence of refractive index n_0 and birefringence Δn are shown in Fig. 2. Dispersions of n_0 and n_e can be successfully approximated by the single-effective-oscillator model [11],

$$n^2 - 1 = \frac{E_{\mathrm{d}} E_0}{E_0^2 - E^2}, \tag{3}$$

with the values of E_{d} and E_0 equal to 28.5, 3.67 eV and 27.8, 3.81 eV for n_0 and n_{e}, respectively. The linear birefringence Δn can also be described on the basis of (3), but the corresponding single-oscillator energy (2.87 eV) does not reveal any particular optical transition responsible for the optical anisotropy effect. The validity of the single-oscillator approximation for CdP$_2$ is confirmed by the agreement between the values of E_{d} and E_0 mentioned above and those calculated from the Kramers-Kronig analysis of the reflection spectra [10]. The latter values were determined using the relationships [11] between E_{d}, E_0 and the r-th moments of the spectra of the imaginary part of the dielectric constant $\varepsilon_2(E)$, $M_r = (2/\pi) \int\limits_0^\infty E^r \varepsilon_2(E)\,\mathrm{d}E$.
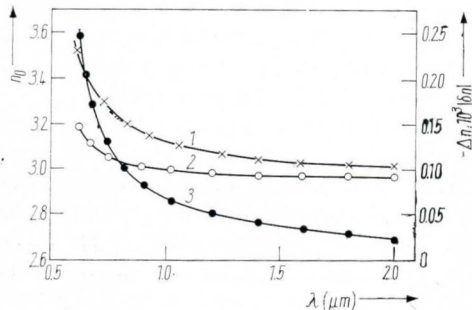

Fig. 2. Experimental (points) and calculated (solid lines) spectra of ordinary refractive index n_0 (1), linear Δn (2), and circular δn (3) birefringence

4. Discussion

The optical properties of CdP_2 can be discussed on the basis of semiempirical models [4, 7, 11] taking into account the peculiarities of the crystal structure of the compound.

The tetragonal CdP_2 crystal satisfies the general valence rule [12] and is a polyanionic compound. Though the anions P(1) and P(2) occupy crystallographically nonequivalent sites, all the atoms have nearly tetrahedral coordination [1]. Therefore, studying the spectroscopic properties of CdP_2, slightly distorted tetrahedra as structural units and the two types of bonds, Cd–P and P–P, have to be considered.

Analyzing the optical activity of crystals, it is useful to examine the irreducible components of the third-rank tensor of optical activity η [13]. The pseudoscalar part $\eta^{(0)}$ represents the molecular contribution to the rotatory power and is expressed as $\eta^{(0)} = 1/3(g_{33} + 2g_{11})$ e (e is the antisymmetrical third rank unit tensor) for crystals of symmetry class D_4 [7]. The structural rotatory power is characterized by $\eta^{(2)} = 2/3(g_{33} - g_{11})$ e. The experimental results show that the ratio $|g_{33}/g_{11}| \neq 2$ and varies slightly with wavelength. Therefore, the molecular contribution in CdP_2 does not vanish. This is a case similar to the benzile crystals and opposite to that of quartz [7].

Thus, the optical activity in CdP_2 has both molecular and structural contributions. This is in agreement with the symmetry of the structural units. The tetrahedra formed by the nearest neighbours of Cd, P(1), and P(2) atoms are slightly distorted [1]. The distortion causes the decrease of the T_d symmetry and thus enantiomorphism of the structural unit may be allowed.

The nearly tetrahedral coordination of atoms allows to compare the spectroscopic parameters in CdP_2 with those in the other tetrahedrally bonded binary and ternary semiconductors.

The dispersion energy E_d obtained from the spectra of refractive indices is known [11] to be related with the cation coordination number N_c, formal anion valency Z_a, and the effective number of valence electrons per anion N_e,

$$E_d = \beta N_c Z_a N_e . \tag{4}$$

The parameter β calculated from the experimental values of E_d is equal to 0.40 eV for n_0 and 0.39 eV for n_e. These values are close to the "covalent" value $\beta_c = (0.37 \pm 0.05)$ eV for the tetrahedrally bonded $A^N B^{8-N}$ zincblende and the diamond-type structures. Then the ionicity of the crystal f_i [4] can be evaluated by means of the empirical relation [13]

$$E_d = \frac{60}{\sqrt{2}} (1 - f_i)^{1/2} \tag{5}$$

which is valid for the materials with covalent structures. The mean value of $f_i = 0.56$ shows the ionicity of CdP_2 crystals being close to that of A^2B^6 compounds and higher than f_i of A^3B^5 semiconductors [4].

The spectroscopic parameters of the $A^2B^4C_2^5$-type compounds are usually considered to be composed of two contributions from the bonds A^2–C^5 and B^4–C^5 [15]. The fractional ionicity of the Cd–P bond is approximately constant in all the $A^2B^4C_2^5$ semiconductors and is equal to 0.54. This value is close to that obtained for CdP_2.

In $A^2B^4C_2^5$ compounds the linear birefringence is mainly determined by the A–C bond [16]. Following [16], the birefringence of a crystal is caused by the bond and local field anisotropies. Two invariants of the local field tensor can be computed using the experimental values of the susceptibility tensor components and the microscopic polarizabilities [17]. The local field factor f and the local field anisotropy δf for CdP_2 are equal to 1.5 and -0.051, respectively. Therefore, the contribution of the local field anisotropy to birefringence in CdP_2 has the sign opposite to that in CdB^4P_2-type

semiconductors [16]. This is due to the different ordering of the Cd–P bonds in compounds of D$_4^4$ and D$_{2d}^{12}$ symmetries.

Thus, the spectroscopic properties of CdP$_2$ are mainly determined by the Cd–P bonds. The P–P bonds, responsible for the structure of the energy levels in the lower part of the valence band [18] are important at higher energies and can be neglected interpreting the dispersion of the optical constants in the region of transparency.

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