SOLID SOLUTIONS OF THE $AgCd_2GaS_4$—$AgCd_2GaSe_4$ SYSTEM, THEIR ELECTRIC AND PHOTOELECTRIC PROPERTIES

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Solid solutions of the $AgCd_2GaS_4$—$AgCd_2GaSe_4$ system are photosensitive materials with a photoconductivity maximum in a spectral region of 510—810 nm, the position of which depends on the solution composition . By physical properties, those solid solutions are similar to their electron analogs, CdS—CdSe alloys. In specimens with 30—50 mol.% of $AgCd_2GaSe_4$, similarly to binary semiconductor alloys, an abrupt change of the energy position of centers, which are responsible for the optical activity of specimens, is observed. We suggest that those centers are Ag_{Cd}^- and Ga_{Cd}^+, whose parameters depend on the nature of anion environment.

1. Introduction

An important task of modern materials science is the creation of new inexpensive multicomponent semiconductor materials, the physical properties of which can be controlled by varying their composition. Such materials include, in particular, solid solutions of the complex compounds of chalcogenide semiconductors.

When studying the phase diagrams of the $AgGaS_2$—CdS [1] and $AgGaSe_2$—CdSe [2] systems, two new quaternary phases, $AgCd_2GaS_4$ and $AgCd_2GaSe_4$, respectively, have been revealed. The latter are isostructural and crystallize in a rhombic structure (the space group $Pmn2_1$) (see the table).

The similarity of crystal structures and formula contents of $AgCd_2GaS_4$ and $AgCd_2GaSe_4$ compounds, which are electronic analogs to CdS and CdSe, respectively, evidences for an opportunity for them to make up solid solutions with a wide interval of relative content. It has been confirmed while studying a ternary mutual system $AgGaS_2 + 2CdSe \Leftrightarrow AgGaSe_2 + 2CdS$ [4], the cross-section $AgCd_2GaS_4$—$AgCd_2GaSe_4$ being its part. A substitution of selenium for sulfur in this solid solution, provided the constant content of cations, has to induce a gradual modification of its physical and chemical properties. The authors of work [4] demonstrated that the solid solutions of the $AgCd_2GaS_4$—$AgCd_2GaSe_4$ system crystallize, as their components do, in a rhombic structure. Moreover, Cd cations occupy certain crystallographic positions, while the distribution of Ag and Ga atoms is stochastic. The anions (S and Se) stochastically occupy the positions of S atoms in the structure of $AgCd_2GaS_4$. Therefore, the structure of the $AgCd_2GaS_4$—$AgCd_2GaSe_4$ solid solutions can be described as a close packing of chalcogene atoms, where half the tetrahedral cavities are occupied by cations. Every anion is surrounded by four cations and, vice versa, every cation is surrounded by four anions. A stochastic character of the cation (Ag, Ga) and anion (S, Se) arrangements at the crystal lattice sites evidences for a disordered structure, where the long-range order is violated, which causes the appearance of tails of the density of states in the energy gap [5,6].

2. Experimental Results and Their Discussion

For studying the physical properties of the solid solutions of the $AgCd_2GaS_4$—$AgCd_2GaSe_4$ system, 13 samples of different contents of components that changed with steps of 5 or 10 mol.% have been fabricated. Alloys were synthesized from highly pure

Crystallographic parameters of CdS, CdSe, $AgCd_2GaS_4$, and $AgCd_2GaSe_4$ compounds

Compound	Structure	Space group of symmetry	Lattice parameters, nm			Source
			a	b	c	
CdS	hexagonal	$P6_3mc$	0.41348	—	0.67490	[3]
CdSe	hexagonal	$P6_3mc$	0.4309	—	0.7021	[3]
$AgCd_2GaS_4$	rhombic	$Pmn2_1$	0.81459	0.68989	0.65932	[1]
$AgCd_2GaSe_4$	rhombic	$Pmn2_1$	0.84049	0.71934	0.68434	[2]
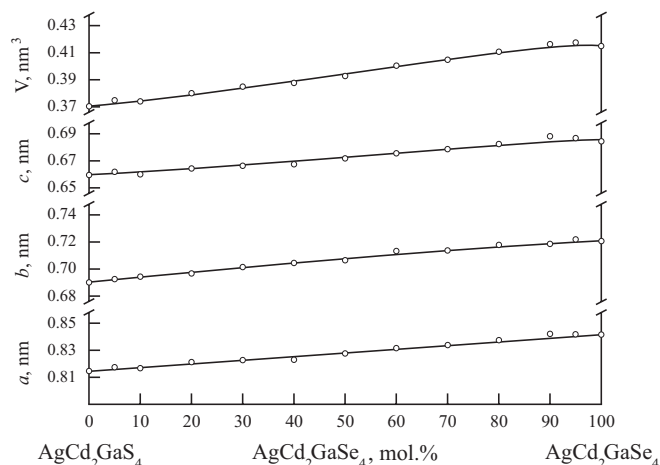
Fig. 1. Lattice periods and the elementary cell volumes of $AgCd_2GaS_4$–$AgCd_2GaSe_4$ alloys

Fig. 2. (*a*) Dependence of the specific conductivity σ of the $AgCd_2GaS_4$—$AgCd_2GaSe_4$ solid solutions at 293 K on their component content. (*b*) Temperature dependence of the specific conductivity of the solid solution 60 mol. %-$AgCd_2GaS_4$— 40 mol. %-$AgCd_2GaSe_4$

elements with a grade not less than 99.99 wt.%. The calculated weights of elements were placed into quartz ampoules, which were pumped out and sealed off. In the first stage, the ampoules were heated up in the flame of an oxygen–gas torch until elementary sulfur had been bound completely. Then, containers were placed into a shaft furnace and heated up at a rate of $40 - 50$ K/h. The maximal temperature of the synthesis depended on the percentage content of components, but did not exceed 1420 K. After the specimens had been held on a vibration table for 6–10 h at the corresponding maximal temperature, they were cooled down to 870 K at a rate of 10 K/h. At this temperature, the alloys were held for 500 h and then quenched with cold water. The fabricated alloys were studied using the X-ray phase analysis at a DRON 4—13 diffractometer (CuKα emission). The calculations of the elementary cell periods of the alloy phases were made with the use of the PDWin2 software package. They testified that an unlimited series of solid solutions, based on a quaternary compounds, emerges at 870 K. An almost linear increase of the periods of elementary cells of the investigated alloys, which accompanies the increase of the $AgCd_2GaSe_4$ content (see Fig. 1), agrees well with the values of chalcogene ion radii and with the dependence obtained in work [4].

For the obtained alloys, we studied also the temperature dependences of the specific conductivity σ, the thermal emf coefficients S, and the spectral distributions of the photoconductivity $\Delta\sigma$. The specimens were formed as rectangular parallelepipeds with dimensions of $(0.2 \div 0.4) \times (1 \div 2) \times (3 \div 5)$ mm^3. The surfaces of the specimens were ground and polished
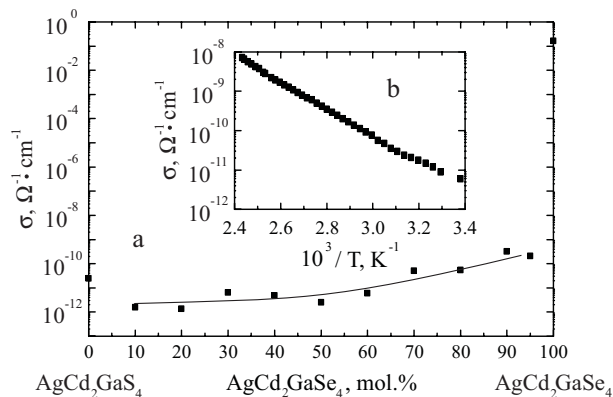
with diamond pastes, which was followed by surface etching in a solution of HNO_3 with a 10% addition of H_2O_2. The leads for electrical measurements were mounted onto the sample surfaces with the help of electric-arc welding. Occasionally, the contacts of the gallium–indium eutectic were produced through its rubbing in the specimen surface. The ohmic behavior of contacts persisted in wide intervals of temperature and voltage.

Fig. 2,*a* demonstrates the dependence of the dark electroconductivity of solid solutions on their composition obtained at 293 K. The initial components of the solution ($AgCd_2GaS_4$ and $AgCd_2GaSe_4$), according to the signs of their thermal emf coefficients S, belong to semiconductors of the n-type, with $S \approx 500$ and 300 μV/K, respectively. The solid solutions of various compositions also turned out compounds with the conductivity of the n-type. The values of the specific conductivity of $AgCd_2GaS_4$— $AgCd_2GaSe_4$ solid solutions were lower than those of their components within the whole interval of composition under investigation (Fig. 2,*a*).

The small value of σ (10^{-11}—10^{-10} $\Omega^{-1}cm^{-1}$), which grows to some extent if the content of $AgCd_2GaSe_4$ increases (may be owing to a reduction of the energy gap), testifies to that all $AgCd_2GaS_4$—$AgCd_2GaSe_4$ solid solutions belong to the defective, compensated semiconductors with a Fermi level E_F lying deeply within the energy gap, which is confirmed by a small value of the thermal emf coefficient $S = 100 \div 200$ μV/K for various specimens. Such values for S

are typical of compensated semiconductors with close contributions of the electron and hole components to the electroconductivity.

The AgCd$_2$GaS$_4$ compound melts incongruently and possesses a region of homogeneity [1]. So, if the single crystals are grown, using the solution-melt method, from initial compositions that correspond to a region of primary crystallization, a variation of the crystal composition, namely, a reduction of the CdS content and an increase of the AgGaS$_2$ one, along the boule length is to be expected. As a result, some Cd sites of the crystal lattice are occupied by Ag and Ga atoms, which is also corroborated by results of the microprobe analysis executed for three points of the single-crystal boule. Ag atoms, which replace cadmium atoms at the sites of the cation sublattice (Ag$_{Cd}^-$), are well-known acceptor centers in CdS single crystals (electron analogs of AgCd$_2$GaS$_4$) and play a role of slow recombination centers. Centers Ga$_{Cd}^+$ are donors that compensate the charge of acceptors. The energy position of an Ag$_{Cd}^-$ center in AgCd$_2$GaS$_4$, $E \approx E_v + 1.2$ eV, was found in work [7] by analyzing the optical quenching of photoconductivity. The similar situation may take place in solid solutions, where Ga$_{Cd}^+$ centers play the role of majority donors, while Ag$_{Cd}^-$ ones do the role of acceptors.

The results of experimental researches evidence for the presence of structural defects of a wide spectrum in multicomponent compounds. Therefore, in addition to the mentioned majority defects, the structural defects connected to vacancies, interstitial atoms, their complexes, and so on may exist. It should be noted that, in ternary chalcogenide compounds A^{I}B^{III}C$_2^{IV}$, the majority defects are the centers A$_B$ and B$_A$ [8,9] which are close by their type to defects in the AgCd$_2$GaS$_4$—AgCd$_2$GaSe$_4$ solid solutions.

Fig. 2,b displays the temperature dependence of the static electroconductivity σ of one of the studied alloys. Analogous dependences were also observed for the solid solutions of different compositions. As it stems from this figure, the temperature dependence $\sigma(T)$ of the AgCd$_2$GaS$_4$—AgCd$_2$GaSe$_4$ solutions is described well in the temperature interval $T \geq 350$ K by the exponential dependence typical of disordered or strongly defective compensated semiconductors [5,6],

$$\sigma = C_0 \exp\left(-\frac{E}{kT}\right), \qquad (1)$$

where the values of C_0 are within the interval 80—120 Ω^{-1}cm^{-1} for various alloys. The energies of conductivity activation determined from formula (1) for

solutions of various compositions fall within an interval $E \approx 0.7 \div 0.8$ eV. The value of C_0 close to 10^2 Ω^{-1}cm^{-1} testifies [6] to that, for disordered semiconductors, the mechanism of conductivity consisting in the thermal excitation of electrons from the levels close to the Fermi level situated in the energy gap onto the current level in the conduction band takes place. If it is true,

$$E = E_c - E_F, \qquad (2)$$

where E_c is the energy of a current level in the conduction band.

Spectral distributions of photoconductivity for alloys of various compositions are shown in Fig. 3.

Fig. 4 confronts the dependence of the energy position of the maximum of photoconductivity in AgCd$_2$GaS$_4$—AgCd$_2$GaSe$_4$ solid solutions on their composition (curve 1) with the content dependence of the energy of hole ionization in CdS—CdSe alloys from the centers of slow recombination in them (curve 2). The last point on curve 1, which corresponds to AgCd$_2$GaSe$_4$ compound, was taken from work [10]. Curve 2 was taken from work [11].

It follows from Fig. 3 (curve 1) that the AgCd$_2$GaS$_4$ specimen is characterized by a broad photoconductivity maximum which is situated near the edge of intrinsic absorption and includes two overlapping bands I and II. Several other specimens manifest an additional band near 600 nm. The energy positions of the maxima of those bands are depicted in Fig. 4. It is worth noting that our results agree well with the results obtained in [7]. Photoconductivity band I may be connected with intrinsic optical transitions. The energy gap of the AgCd$_2$GaS$_4$ compound evaluated from the maximum of band I amounts to 2.43 eV, which is in a good agreement with the data in [7]. The formation of AgCd$_2$GaS$_4$—AgCd$_2$GaSe$_4$ solid solution results in a significant reduction (by more than an order of magnitude) of the intrinsic photosensivity of specimens, which is surely connected with the increase of crystal imperfection. The impurity-induced photoconductivity is dominant in solid solutions, with the maximum position of impurity-induced photoconductivity III at $\lambda_{max} \approx 640$ nm ($h\nu \approx 1.9$ eV) in alloys with AgCd$_2$GaSe$_4$ contents below 30 mol.% (Fig. 3, curve 2) being practically independent of the composition (Fig. 4, curve 1). In alloys with the content of 30—50 mol.% of AgCd$_2$GaSe$_4$, a drastic reconstruction of photoconductivity spectra takes place. Near to maximum III, there appears a photoconductivity maximum IV ($\lambda_{max} \approx 700$ nm), which, by overlapping with the former, creates a broad impurity-induced band of photoconductivity (Fig. 3,

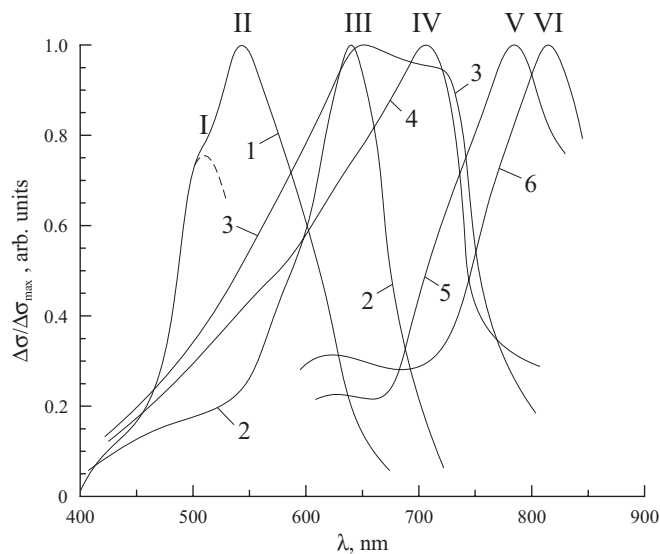Fig. 3. Spectral distributions of photoconductivity of the $AgCd_2GaS_4$—$AgCd_2GaSe_4$ alloys with various contents of the $AgCd_2GaSe_4$ component: 0 , 10, 30, 40, 60, and 80 mol.% (curves 1-6, respectively). $T = 293$ K

Fig. 4. Dependence of the energy position of the maximum of photoconductivity in alloys of the $AgCd_2GaS_4$—$AgCd_2GaSe_4$ system on their composition (1) and the content dependence of the energy of hole ionization in CdS—CdSe alloys from the centers of slow recombination to the valence band (2)

curve 3). Further increase of the $AgCd_2GaSe_4$ content leads to a reduction of the intensity of maximum III and to the isolation of maximum IV (Fig. 3, curve 4), which shifts towards the long-wave range up to $\lambda_{max} \approx 760$ nm (maximum V, $h\nu \approx 1.6$ eV) for the 50-mol.% $AgCd_2GaSe_4$ alloy and then little changes its position for the solutions with higher $AgCd_2GaSe_4$ contents (Fig. 3, curves 5 and 6; Fig. 4, curve 1).

As is seen from Fig. 3, any spectral distribution curve of photoconductivity has a background on its short-wave side, which may be due to the intrinsic photoconductivity of the alloy. However, a low intensity of the background and its smearing do not give an opportunity to use the intrinsic photoconductivity data for the estimation of the energy gap width in the $AgCd_2GaS_4$—$AgCd_2GaSe_4$ solid solution as a function of its content.

Binary wide-band-gap semiconductors of $A^{II}B^{VI}$ group and, in particular, CdS and CdSe, are electron analogs of $AgCd_2GaS_4$ and $AgCd_2GaSe_4$ compounds. The alloys ZnS—CdS, CdS—CdSe, and ZnS—ZnSe were intensively studied in the middle of the last century [11—14] and were widely adopted as phosphors in different electrooptical transducers. It was demonstrated that if Zn cations in alloys of the ZnS—CdS system are substituted by Cd ones, then, owing to the increase of the CdS content, there occurs a gradual reduction of the
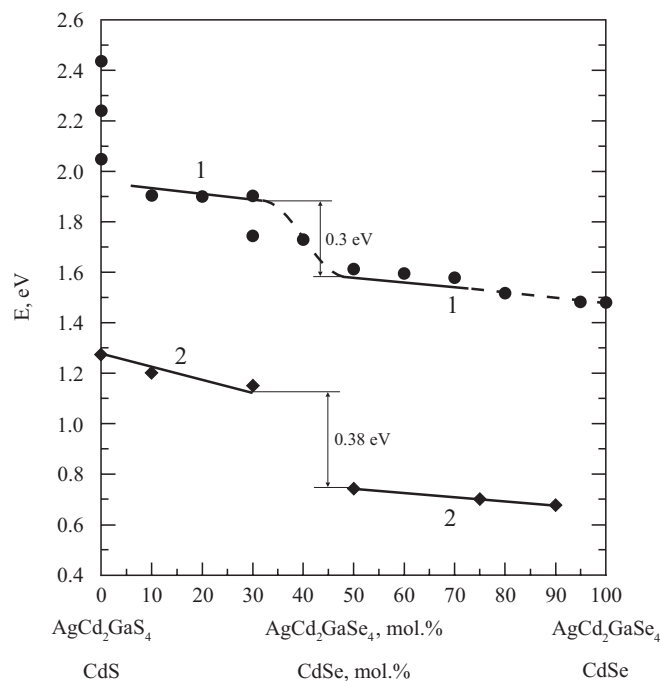
energy gap width, provided the energy position of acceptors connected with the emission centers remains constant with respect to the valence band [12]. Emission centers in binary semiconductors behave differently, if anions are substituted, e.g. S by Se, in solid solutions of the CdS—CdSe and ZnS—ZnSe systems. The emission spectra of ZnS—ZnSe alloys activated with Cu or Ag are very similar to the photoconductivity spectra of ZnS—CdS solid solutions [11, 12] and the $AgCd_2GaS_4$—$AgCd_2GaSe_4$ system under investigation. In ZnS—ZnSe alloys with the content of ZnSe within the range 30—50 mol.%, the emission maximum is drastically shifted towards the long-wave side of the spectrum, with two new bands emerging. As the Se content grows further, only one long-wave emission band persists. It is explained by the fact that if an anion in the vicinity of an emission center is substituted, the ionization potential of the center and, correspondingly, its position with respect to the valence band change [12]. Curve 2 in Fig. 4 presents the dependence of the optical energy of hole ionization from acceptors, which play a role of the centers of slow recombination in CdS and CdSe

compounds, on the content of CdS—CdSe alloys [11]. The similarity of the behavior of the impurity-induced photoconductivity spectra of $AgCd_2GaS_4$—$AgCd_2GaSe_4$ solid solutions, the emission spectra of alloys of binary semiconductors, and the dependence of the energy of hole ionization from the centers of slow recombination in CdS—CdSe alloys on their content (Fig. 4, curves *1* and *2*), testify to that defects of such types are responsible for the quoted phenomena in the solutions mentioned above.

As is known [14], Cd vacancies in CdS and CdSe compounds, or Ag^-_{Cd}-centers surrounded by four nearest anions (in solutions, those are S and Se atoms) in the case of Ag-doped specimens, play a role of slow recombination centers.

In work [7], the energy position of an acceptor center Ag^-_{Cd} in $AgCd_2GaS_4$ was shown to equal $E \approx E_v + 1.2$ eV, which is close to that in CdS. Therefore, those centers cannot be responsible, obviously, for the impurity-induced photoconductivity in the studied alloys, where the spectral positions of photoconductivity maxima are determined by a much higher energy.

In our opinion, the Ga^+_{Cd} centers can fulfill the role of impurity-induced photoconductivity centers in the solutions. In the crystal lattice of a solid solution, such a center (a cation) is surrounded by the nearest anions (S and Se). Occupying the energy position above the Fermi level E_F, it is in the ionized state. The photo-induced transitions of electrons from the valence band onto Ga^+_{Cd} centers stimulate the maximum of impurity-induced photoconductivity in $AgCd_2GaS_4$—$AgCd_2GaSe_4$ alloys. If the content of $AgCd_2GaSe_4$ grows, more and more S anions around the Ga^+_{Cd} center are substituted by Se anions, and, in a certain interval of the solution composition (30—50 mol.% of $AgCd_2GaSe_4$), there is an abrupt variation of the ionization energy of the Ga^+_{Cd} centers, as it occurs in alloys of binary semiconductors [11–14] (Fig. 4, curve *2*).

As is known, the effective coefficient of the thermal emf in a simple system with current carriers of two types is determined according to the formula

$$S = \frac{S_p\sigma_p + S_n\sigma_n}{\sigma_p + \sigma_n}, \qquad (3)$$

where S_p, S_n, σ_p, and σ_n are the "partial" thermal emfs and specific electroconductivities of the hole and electron components, respectively, ($S_p > 0$, $S_n < 0$). Therefore, we may expect that as the hole concentration in the valence band would increase, the value of S governed by the photo-induced transitions of electrons onto Ga^+_{Cd} centers should diminish. The thermal emf measurements

in $AgCd_2GaS_4$—$AgCd_2GaSe_4$ solid solutions with the conductivity of the n-type, carried out both in darkness and under illumination of the specimens with light, the wavelength of which corresponds to the maximum of photoconductivity, confirmed the fact of the reduction of the S value in the majority of the illuminated specimens of solid solutions.

It should be noted that the ratio factor $k = \sigma_L/\sigma_D$ of the conductivity variation at illuminating the specimen by light with the quantum energy that corresponds to the maximum of photoconductivity, measured at the light illuminance $E \approx 100$ Lx and the temperature $T \approx 293$ K, was practically constant ($k \approx 20 \div 25$) for solutions of various contents. The time of photoconductivity relaxation τ, i.e. the time interval after the termination of excitation, when the conductivity became e times lower, was at that the largest for $AgCd_2GaS_4$ compound ($\tau \approx 120 \div 150$ s), with the attributes of the remnant or frozen conductivity being observed. For all the other specimens of the $AgCd_2GaS_4$—$AgCd_2GaSe_4$ solid solutions, it amounted to $\tau \leq 4$ s.

Thus, the alloys of the $AgCd_2GaS_4$—$AgCd_2GaSe_4$ system obtained by us are similar by physical properties to their electron analogs, the alloys of the CdS—CdSe system. They are photosensitive materials with a maximum of photoconductivity which falls within the range of 510—800 nm and depends on the percentage content of components in the system.

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ТВЕРДІ РОЗЧИНИ СИСТЕМИ $AgCd_2GaS_4$—$AgCd_2GaSe_4$, ЇХ ЕЛЕКТРИЧНІ І ФОТОЕЛЕКТРИЧНІ ВЛАСТИВОСТІ

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Р е з ю м е

Тверді розчини системи $AgCd_2GaS_4$—$AgCd_2GaSe_4$ є фоточутливими матеріалами з максимумом фоточутливості у діапазоні 510—810 нм, положення якого визначається складом розчину. За фізичними властивостями такі тверді розчини подібні до своїх електронних аналогів — сплавів системи CdS—CdSe. У зразках, в складі яких 30—50 мол.% $AgCd_2GaSe_4$, спостерігається різка зміна енергетичного положення центрів, відповідальних за їхню оптичну активність, як і в сплавах бінарних напівпровідників. Вважається, що такими центрами є Ag_{Cd}^- і Ga_{Cd}^+, параметри яких залежать від природи аніонного оточення.