ISSN 0016-7029, Geochemistry International, 2007, Vol. 45, No. 11, pp. 1146–1151. © Pleiades Publishing, Ltd., 2007.
Original Russian Text © V.L. Tauson, N.V. Smagunov, V.A. Datkov, T.M. Pastushkova, 2007, published in Geokhimiya, 2007, No. 11, pp. 1239–1244.

SHORT COMMUNICATIONS

Mechanism of Au Incorporation into Cd Sulfide: Evidence from Au Partition between CdS and Ag_2S

V. L. Tauson, N. V. Smagunov, V. A. Datkov, and T. M. Pastushkova

Vinogradov Institute of Geochemistry, Siberian Branch, Russian Academy of Sciences,
ul. Favorskogo 1a, Irkutsk, 664033 Russia
e-mail: vltauson@igc.irk.ru

Received October 24, 2006

DOI: 10.1134/S0016702907110080

INTRODUCTION

In our earlier publications [1, 2], we attracted attention to endocrypty as a phenomenon of the incorporation of atoms of an admixed element into the real structure of the host crystal, with this phenomenon possibly responsible for the significant enrichment of mineral phases in trace elements. Compared to the role of classic isomorphism, that of endocrypty remains, however, obscure. This issue should be discussed with regard for the following facts. First, defects that make it possible for an admixture to enter the structure of a crystal cause an increase not only in the limiting concentration of this minor element [2] but also in its partition coefficient between the phases. In geochemical literature, this was first established for point defects in [3] and was then extended to other types of defects [4]. For these systems, it was proposed to differentiate between true phase coexistence, which refers to an isomorphic (in the strict sense) admixture in a crystal, and apparent phase composition correlation, which is characterized by an elevated partition coefficient of an admixture due to its interaction with defects [4, 5]. In the former instance, the partition coefficient can be calculated from thermodynamic data for the corresponding isomorphic series, whereas an analogous calculation applicable to the latter situation only with regard of the properties of the determinative defects [4]. Obviously, the value of the so-called trapping effect [3], i.e., a relative increase in the partition coefficient, can vary depending on the nature and concentrations of the defects, which differently react to variations in the external and internal parameters of state of the system. Second, in the case of endocrypty, the postcrystallization history of the admixture should differ from that of traditional isomorphic admixture. In a closed system, the history of an isomorphic series is completely controlled by the temperature and pressure evolutionary paths, whereas the situation with endocrypty is more complicated, even if it is related to equilibrium defects, for example, thermal or constitutional (structural) vacancies. The system can pass into the state of forced equilibrium [4, 6], in which it is maintained by internal forcing factors. Examples of these states were discussed in [4]. One of the compelling factors may be the balance of the chemical energy of compositional fluctuations and the short-range ordering of vacancies (Cu_5FeS_4–$Cu_{2-x}S$, $Fe_{1-x}S$, and others). In this situation, phase exsolution can be avoided, and no admixture will be exsolved as an individual phase at changes in the P–T conditions, or the character of the transformations will be inadequate to these changes compared to that of a normal isomorphic admixture. Thus, a real crystal can not only “trap” a minor element in an elevated concentration but also retain this concentration via establishing forced equilibria of various types. The qualitative aspect of this problems seems to be obvious, whereas the possibility of its quantitative description remains obscure because some elements “prefer” to occur as isomorphic admixtures in certain crystalline matrices, whereas others are, conversely, associated with defects. In this paper, the problem discussed above is considered using the example of Au incorporation into greenockite, a hexahonal modification of Cd sulfide, in the course of Au partitioning between coexisting CdS and Ag_2S.

MATERIALS

Greenockite was used as a reference mineral in constructing phase correspondence diagrams and determining the limits of Au incorporation in various phases of sulfide systems. The mineral is characterized by an even distribution of the element, a feature typical of a structural admixture, which was confirmed by specialized research [7]. The limiting Au concentrations in greenockite were estimated at 50 ± 10 ppm at 500°C and 10 ± 2 ppm at 450°C and a 1 kbar pressure, which indicates that mixing is more strongly dependent on temperature compared to that in the regular solution [8]. The incorporation mechanism was not explored in detail. Greenockite was utilized in our research as an examined mineral, and the reference mineral was argentite (α-Ag_2S), which forms substitution solid solution with Au sulfide within a broad temperature and compositional ranges. According to the phase diagram [9], argentite is a disordered phase with a body-centered unit cell and contains up to 33 mol % (and more) AgAuS at temperatures of 300°C and higher. At higher Au concentrations, the solid solution is characterized by a primitive cubic cell because of a second order phase transition. Argentite is stable at temperatures higher than 175 ± 2°C and is an unquenchable phase that transforms into monoclinic acanthite (β-Ag_2S) below this temperature. This transition cannot affect the concentration of the Au end member in the crystals at its low values (i.e., near the ordinate of the pure Ag_2S component). A temperature decrease and the passage over the eutectoid isotherm (113°C) gives rise to the association of β-Ag_2S and tetragonal β-Ag_3AuS_2. Argentite seems to be a promising reference mineral, because the isomorphic character and valence state of Au in it provoke no doubt. The occurrence of Au in this mineral, largely in the form of Au(I), is also confirmed by the results of our research.

EXPERIMENTAL AND ANALYTICAL TECHNIQUES

The experiments were conducted on conventional equipment for thermogradient hydrothermal synthesis [8]. Samples 6 g in mass and consisting of chemically pure CdS and Ag_2S in the proportion 1 : 1 and a minor amount (1 wt %) of Au foil (99.99% Au) folded as a cornet were placed into titanium (alloy VT-6) insert vessels ~50 cm^3 in volume with preliminarily passivated inner surface. In order to vary the Au amount in the phases, we used various NH_4Cl-based solvents with added Na_2S, NaOH, or HCl. The total concentration of the mineralizers was always the same (the filling coefficient of the insert vessels under a 1 kbar pressure was calculated for 10% NH_4Cl). The insert vessels were placed into autoclaves of stainless steel and held for 3 days at 450°C to homogenize the material of the experimental samples and then for 9 days at a temperature gradient (10°C along the outer wall of the autoclave). The experiments were terminated by quenching the autoclaves in cold running water.

The experimental products were examined by X-ray powder diffraction (XRPD; DRON-3 diffractometer, CuK_α radiation, Ni filter) and X-ray photoelectron spectroscopy (XPS; LAS-3000 spectrometer manufactured by Riber, AlK_α = 1486.6 eV, emission current 20 mA, accelerating voltage in the tube 10 kV, vacuum in the analytical chamber 5×10^{-10} torr, calibration against C 1s carbon line with a binding energy of 285 eV). The samples were pulverized and introduced into the spectrometer chamber immediately before their spectroscopic examination. The Au $4f_{7/2}$-$4f_{5/2}$ doublet was registered. The binding energy of the components of the doublet and the peak areas were calculated by a computer program designed for the processing of spectra with regard for the nonlinear background and the Lorentz–Haussian shapes of the peaks. In order to identify various Au modes, we applied the technique of statistical treatment of analytical data for single crystals (STADSC), which was described in detail elsewhere (see [8, 10] and references therein). The chemical analyses of single crystals for Au was conducted by electrothermal atomic absorption on a Perkin-Elmer M 503 spectrometer. In compliance with the requirements of the STADSC procedure, we analyzed sets of 20 carefully selected single crystals of each of the phases: CdS and Ag_2S. The Au detection limit was 0.2 ppb, the precision was ±10%.

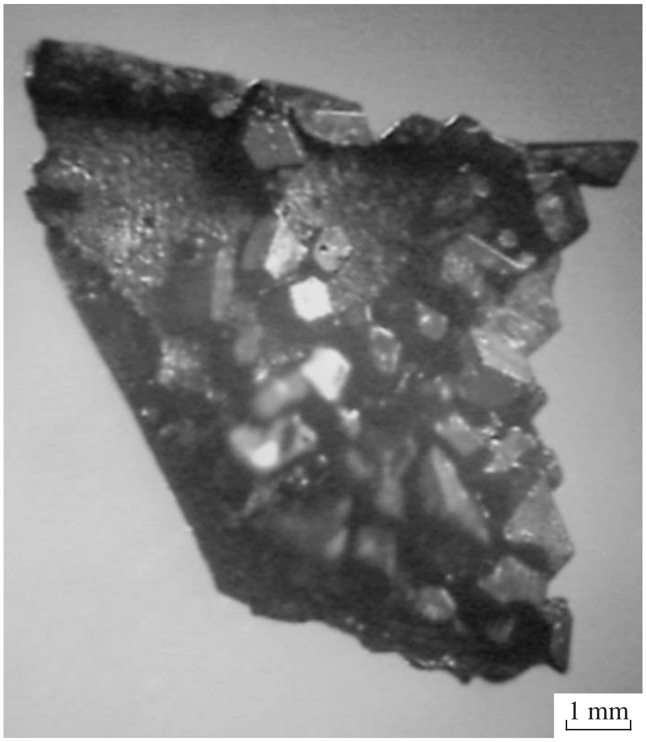

Fig. 1. Ag_2S crystals on gold foil replaced by this phase.

RESULTS

The greenockite crystals synthesized in our experiments are 1.5–2 mm long and have a pinkish brown to orange red color and prismatic dipyramidal habitus typical of the hexagonal system. The dark Ag_2S crystals are of two types: hexagonal platelets up to 2 mm across and ~0.1–0.2 mm thick and equant crystals up to 1 mm. The latter were found mostly in the starting batch. In solutions containing Na_2S or NaOH, they replaced the material of the gold foil and formed typical cubic crystals on its surface (Fig. 1). The results of X-ray diffraction analysis indicate that gold was completely replaced by silver sulfide in both experiments (2 and 3) with the development of polycrystalline pseudomorphs inheriting the original cornet shape of the foil (Fig. 2). The foil was, however, preserved in other experiments, although

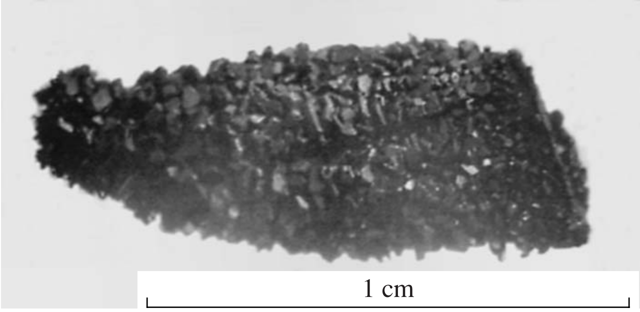

Fig. 2. Complete polycrystalline Ag_2S pseudomorph after gold foil folded into a cornet (experiment 2).

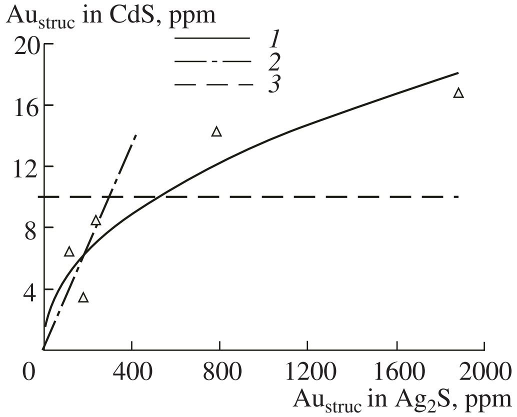

Fig. 3. Partition of an Au structural admixture between CdS and Ag_2S at 450°C and 1 kbar pressure (STADSC results).
(*1*) Approximation of experimental data;
(*2*) linear approximation of points <10 ppm Au in CdS ($K_{Au}^{Gr/Agt}$ ~ 0.03);
(*3*) Incorporation limit of Au in CdS [8, 10].

it was corroded. Ag_2S crystals of both platy and equant shape were very soft and plastic and were not broken but spread when pressed by metallic spikes like plasticine. Both X-ray powder diffraction and chemical analyses indicate that platy crystals are not suitable for determining the mode of Au occurrence by the STADSC technique, because these crystals contain fairly much CdS. The crystals displayed skeletal morphologies, which suggested that greenockite was replaced by argentite during the growth of the crystals or, perhaps, that some metastable phase was formed and immediately decomposed into CdS and Ag_2S. We did not examine this phenomenon more closely but arrived at the conclusion that the platelets were not suitable for our purposes, and we had to utilize equant Ag_2S crystals. These crystals were hand-picked mostly from the sample, in which these crystals were larger and have better morphologies. The use of this material put forth the problem of the equilibrium character of the compared phases, because the greenockite crystals were picked up from the uppermost portion, i.e., near the stopper of the insert. However, in autoclaves of the type used in our experiments, a 10°C temperature difference along an outer wall corresponds to an “internal” temperature difference of no more than 3°C or even less with regard for the equalizing action of the insert vessel [11]. This is lower than the daily temperature drift in our experiments (±5°C) and cannot significantly effect an approach to equilibrium in the crystallization process.

The results of treatment of the experimental products by the STADSC technique are summarized in Table 1 and graphically represented in Fig. 3. In the solutions with added Na_2S and NaOH, both the average Au concentrations and the concentrations of structural Au in both phases are much higher than in the crystals obtained from more acidic solutions. The phase composition correlation diagram (Fig. 3) resembles the situation proposed for endocrypty [2]. The initial fairly steep slope of the curve corresponds to an Au partition coefficient between greenockite and argentite equal to ~3×10^{-2} (Fig. 3, line *2*), although if the limits for Au incorporation in the phases are assumed at 10^{-3} wt % for CdS

Table 1. Results of experiments on Au partition between greenockite CdS and argentite Ag_2S at a temperature of 450°C and a pressure of 1 kbar

Experiment no.	Starting material composition, wt %			Solution composition, wt %				Au concentration, ppm			
	CdS	Ag_2S	Au	NH_4Cl	Na_2S	NaOH	HCl	CdS		Ag_2S	
								$\bar{c}$*	$\bar{x}_2 \pm \sigma$**	$\bar{c}$*	$\bar{x}_2 \pm \sigma$**
1	49.5	49.5	1	10	–	–	–	17.8	3.5 ± 1.3	1523	184 ± 84
2	49.5	49.5	1	9	1	–	–	143	17.0 ± 4.9	4845	1869 ± 471
3	49.5	49.5	1	9	–	1	–	44.8	14.3 ± 2.0	1987	777 ± 194
4	49.5	49.5	1	9	–	–	1	23.1	6.5 ± 2.8	462	118 ± 20
5	49.5	49.5	1	8	–	–	2	31.3	8.5 ± 3.4	626	236 ± 68

Notes: * Average Au concentration in the statistical sampling.
** Parameter of the STADSC technique [8, 10]: average concentration of evently distributed Au.

and 58.46 wt % for AgAuS, it should be at least three orders of magnitude lower. This decrease is manifested in the gentler slope of the phase composition correlation curve with the Au concentration increasing to $c_{\mathrm{Au}} >$ ~10 ppm, i.e., after the limiting Au concentration in CdS is reached. The initial steep slope of the curve suggests that Au is accommodated at structural defects in CdS, with the concentration of these intrinsic defects comparable with that of the limiting Au concentration. When a normal isomorphic mixture is formed, the partition curve has another configuration [2]. The XPS data (Table 2, Fig. 4) indicate that the greenockite contains no Au, whereas the Ag_2S contains Au in two modes: elemental and monovalent sulfide (binding energy according to [12, 13]). Our XRP and STADSC display a good agreement (within ±10%, compare Tables 1 and 2 for experiment 2), which testifies to the reliable differentiation between the structural and nonstructural modes of Au occurrence by the STADSC technique.

Table 2. Parameters of the 4f Au XPS spectrum in aurian Ag_2S from experiment 2

Photoelectron peak	Binding energy, eV	Mode of Au occurrence*	Au concentration	
			at %**	ppm***
$4f_{7/2}$	84.0	Au(0)	65	3149
$4f_{5/2}$	87.7			
$4f_{7/2}$	84.6	Au(I)	35	1696
$4f_{5/2}$	88.3			

Notes: * According to [12, 13].

** Au(0) + Au(I) = 100%.

*** Average concentration was assumed to be equal to 4845 ppm (Table 1).

DISCUSSION

Inasmuch as the range of the possible Au concentration is fairly precisely reproduced in various experiments at the same temperature and notably depends on it, it is reasonable to suggest that Au is partly accommodated in CdS at thermal defects. The own defects of the phase (vacancies and interstitial atoms) form complexes with introduced atoms of the Au admixture and donor–acceptor pairs, which are typical of group-I elements in $A^{II}B^{VI}$ semiconductors [14]. If the limiting Au concentration of 50 ppm at 500°C and 10 ppm at 450°C (see above) are controlled by the maximum concentrations of defects of this type at corresponding temperatures, then the Boltzmann equation can be used [4] to evaluate the corresponding energy of formation: $g = \frac{T_1 T_2}{T_1 - T_2} R \ln\frac{c_1}{c_2}$, where $T_1 = 773$ K, $T_2 = 723$ K, c_1 and c_2 are the corresponding concentrations, and R is the gas constant. The obtained values of 150 kJ/mol = 1.55 eV is consistent with the enthalpy of formation of Cd interstitials (or chalcogen vacancies) in CdSe (133 kJ/mol), the closest analogue of CdS [15]. Note that the formation of $\mathrm{Cd}_i^{\bullet}\text{–}\mathrm{v}'_{\mathrm{Cd}}$ Frenkel pairs was noted in CdS films at relatively low temperatures and is a thermally activated process, which is accompanied by the shift of atoms in the crystal structure during the phase transition of the metastable cubic form of CdS into its stable hexagonal form [16]. Admixtures in CdS and its solid solutions with other $A^{II}B^{VI}$ compounds are often related to acceptor Cd vacancies [17, 18]. It is difficult to identify the structural setting of Au because of its dualistic behavior (which also pertains to other elements of group I). These elements are formally regarded as acceptors in CdS (for example, $\mathrm{Au}'_{\mathrm{Cd}}$) but are characterized by high diffusion coefficients, which can be explained only by the passage of these elements through CdS in the form of interstitial atoms, i.e., donors ($\mathrm{Au}_i^{\bullet}$). In CdS activated with Au, practically all donors are neutralized via combining in pairs with Cd vacancies at the nearest sites [19]. Accordingly, the $\mathrm{v}'_{\mathrm{Cd}}-\mathrm{Au}_i^{\bullet}$ complex may well serve as a mode of Au accommodation in the situation considered here. A serious argument in favor of the participation of Cd vacancies in Au accommodation is provided by the data in [8, 10] on Au accommodation in pyrrhotite in the presence or absence of CdS. It was demonstrated that the limiting Au concentration in pyrrhotite is practically independent of its composition and is close to 25 ppm at 450°C and a pressure of 1 kbar [10]. At the same time, the Au partition coefficient between greenockite and pyrrhotite depends on the composition of pyrrhotite and, hence, also on the sulfur activity. A consequence of this is the seeming decrease in the limiting Au concentration in pyrrhotite with increasing concentrations of structural vacancies in the mineral. The average values of the partition coefficient $\overline{\mathrm{K}}_{\mathrm{Au}}^{\mathrm{Gr/Po}}$ are equal to 0.4, 0.9, and 5.0 at $\log f_{S_2}$ equal to –16.2 (FeS), –13.4 ($Fe_{0.98}S$),

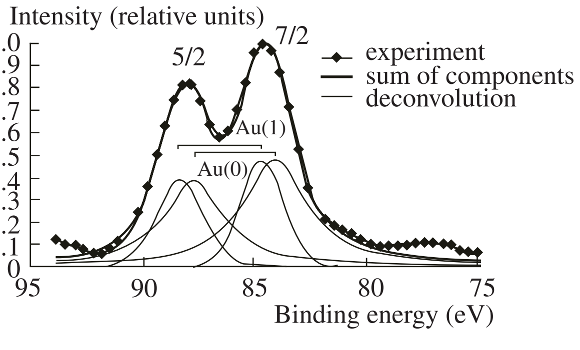

Fig. 4. XPS spectrum Au 4f (experiment 2).

and –5.3 bar ($Fe_{0.87}S$), respectively [8]. The Au partition coefficient increases in favor of CdS with increasing S activity, perhaps, because of an increase in the concentration of Cd vacancies in the greenockite crystals. This effect was not comprehensively explained in [8, 10] because it was determined that Au is incorporated at vacancies, which are contained in pyrrhotite in a concentration three to four orders of magnitude higher than in CdS. It was hard to expect that Au can be incorporated at intrinsic CdS defects, which has a composition very close to the stoichiometric one according to all available data.

A number of plausible mechanisms can be proposed for Au incorporation in CdS with the participation of Cd vacancies, but any of these mechanisms belongs to endocrypty (as understood in [1, 2]) but not true isomorphism, because all of them require the participation of intrinsic defects of the CdS structure. The Au partition coefficient between CdS and Ag_2S is significantly higher (by approximately three orders of magnitude) due to Au interaction with CdS defects compared to the coefficient for purely isomorphic mixtures. This means that endocrypty plays a determining role for incompatible elements, first of all, noble metals, whose isomorphic capabilities in most mineral matrices are very low. The same concentrations of these elements in ideal and real crystals may be reached at concentrations of these elements in the environments differing by several orders of magnitude.

An interesting problem is the postcrystallization history of a trapped admixture. A change in the external conditions leading to a decrease in the concentration of ν'_{Cd} (a decrease in the temperature or sulfur fugacity) should bring about the decomposition of $\nu'_{Cd}–Au^{\cdot}_i$ associates. Using the equation presented above, it can be demonstrated that no more than 0.02 ppm Au should be related to defects already at $T \leq 300°C$. In a regular solid solution with $Q = 65.6$ kJ/mol [8], the isomorphic mixture at the same temperature could contain 1.43 ppm Au. As can be seen, in both variants (both endocrypty and “normal” isomorphic mixture) temperature is the most important factor controlling the Au state in a mineral. The Au diffusion coefficient in CdS at 300°C is ~3×10^{-17} cm^2/s [19]. For defect-free domains of the crystal, which are ~1μm and are obviously larger than blocks in real crystals of hydrothermal sulfides [4], Au atoms can reach the nearest boundary for ~500 days. This means that the Au admixture originally present in the structure can be removed to the inner and outer boundaries of the crystal for a geologically relatively brief time span. This is likely the main tendency in the geochemistry of Au that results in finely disseminated mode of Au occurrence in sulfides known as invisible gold. At the same time, there are possibilities of retaining admixtures in the structure related to both defects of other types (interstitial atoms can be easily incorporated at clusters of line defects [4]) and reactions between point defects (occupation of vacancies $\nu^{2-}_{Cd} + Au^{+}_{i} = Au^{-}_{Cd}$). These mechanisms and the corresponding states of intracrystalline equilibrium are subject for specialized research.

CONCLUSIONS

1. The phenomenon of endocrypty may play a determining role in the incorporation of trace and minor elements in minerals, particularly incompatible elements, whose partition coefficients can increase by a few orders of magnitude compared to the corresponding coefficients for a true isomorphic admixture. This is illustrated by the example of Au in CdS: the partition coefficient of this element between greenockite and argentite $K^{Gr/Agt}_{Au}$ is approximately 10^3 times greater compared to the coefficient expected for the true isomorphic admixture because of Au incorporation at CdS defects (Cd vacancies, supposedly with the formation of $\nu'_{Cd}–Au^{\cdot}_i$ associates).

2. The STADSC technique is reliable and accurate enough not only to enable distinguishing the structural component of an admixture at its trace concentrations but also to obtain additional arguments for validating or invalidating crystal chemical models for the incorporation of admixtures in real crystals.

3. The selection of a reference material for determinative the incorporation limits of admixtures with the use of the phase correspondence principle is a nontrivial problem. The dependence of the concentration of determining defects that interact with the admixture on the activities of components in the gas (fluid) phase results in an apparent phase composition correlation and ambiguous estimates for the incorporation limits of the admixture in the mineral in question. However, if known, the same dependence expands the applicability potential of this mineral in studying defects that control the endocrypty of the trace element in the matrix.

4. The main tendency in the postcrystallization history of Au captured in a mineral is the expulsion of this element to the outer and inner boundaries of the crystal for a geologically relatively brief time span. This is explained by the relatively high Au diffusion coefficient and results in finely dispersed Au in sulfides (so-called invisible gold). The possibility of Au retention in the structure at defects of other types requires further studying.

ACKNOWLEDGMENTS

The authors thank T.S. Krasnoshchekova and L.P. Feoktistova for help in the analytical part of this research, and Yu.V. Shchegol’kov and E.G. Lustenberg are thanked for help in the spectroscopic studies and processing of the results, respectively.

This study was financially supported by the Russian Foundation for Basic Research (project no. 06-05-64171) and the Siberian Branch of the Russian Academy of Sciences (Integration Project 96).

REFERENCES

1. V. L. Tauson, "Endocrypty: Modern Concepts and Investigation Techniques," Geokhimiya, No. 6, 665–668 (1999) [Geochem. Int. **37**, 588–591 (1999)].
2. V. L. Tauson, "Isomorphism and Endocypty: New Approaches to Study of Trace Element Behavior in Mineral Systems," Geol. Geofiz. **40** (10), 1488–1494 (1999).
3. V. S. Urusov and I. F. Kravchuk, "Effect of Incorporation of Microadmixtures by Crystal Lattice Defects and Its Geochemical Significance," Geokhimiya, No. 7, 963–978 (1978).
4. V. S. Urusov, V. L. Tauson, and V. V. Akimov, *Geochemistry of the Solid State* (GEOS, Moscow, 1997) [in Russian].
5. V. L. Tauson, "Problems of Phase Correspondence of Real Crystals in Mineral Systems," in *Mineralogy: Reports of Russian Geologists at the 27th Session of the International Geological Congress* (Nauka, Moscow, 1989), pp. 77–84 [in Russian].
6. V. L. Tauson and V. V. Akimov, "Introduction to the Theory of Forced Equilibria: General Principles, Basic Concepts, and Definitions," Geochim. Cosmochim. Acta **61** (23), 4935–4943 (1997).
7. V. L. Tauson, O. I. Bessarabova, R. G. Kravtsova, et al., "Determination of Binding Forms of Gold on Pyrite by Means of Statistical Analysis." Add Russian Geology and Geophysics, **43**(1), 56–64 (2002).
8. N. V. Smagunov, V. L. Tauson, T. M. Pastushkova, and K. V. Nepomnyashchikh, "Phase Correspondence in Gold Distribution between Concurrently Growing Greenockite and Pyrrhotite Crystals," Geokhimiya, No. 11, 1203–1212 (2004) [Geochem. Int. **42**, 1062–1070 (2004)].
9. J. C. W. Folmer, P. Hofman, and G. A. Wiegers, "Order–Disorder Transitions in the System$Ag_{2-x}Au_xS$ ($0 \leq x \leq 1$)," J. Less-Common Met. **48**, 251–268 (1976).
10. V. L. Tauson, N. V. Smagunov, and T. M. Pastushkova, "Gold Incorporation into Pyrrhotite and the Influence of Nonautonomous Phases on Its Distribution," Geokhimiya, No. 1, 96–100 (2005) [Geochem. Int. **43**, 86–89 (2005)].
11. V. V. Badikov and G. N. Kuznetsov, "Temperature Regime, Heat and Mass Transfer under Free Convection in an Autoclave," in *Materials on Genetic and Experimental Mineralogy* (Nauka, Novosibirsk, 1972), Vol. 7, pp. 174–180 [in Russian].
12. M. J. Scaini, G. M. Bancroft, and S. W. Knipe, "Reactions of AqueousAu^{1+} Sulfide Species with Pyrite as a Function of pH and Temperature," Am. Mineral. **83**, 316–322 (1998).
13. A. M. Widler and T. M. Seward, "The Adsorption of Gold(I) Hydrosulfide Complexes by Iron Sulfide Surfaces," Geochim. Cosmochim. Acta **66** (3), 383–402 (2002).
14. P. I. Baranskii, V. P. Klochkov, and I. V. Potykevich, *Semiconductor Electronics. A Reference Book* (Naukova Dumka, Kiev, 1975) [in Russian].
15. H. Rau, "Nonstoichiometry of ZnSe and CdSe," J. Phys. Chem. Solids **39** (8), 879–882 (1978).
16. R. Lozada-Morales, O. Zelaya-Angel, and G. Torres-Delgado, "Photoluminescence in Cubic and Hexagonal CdS Films," Appl. Surf. Sci. **175–176**, 562–566 (2001).
17. U. V. Desnica, I. D. Desnica-Frankovic, R. Magerle, and M. Deicher, "Compensating Defects and Electrical Activation of Donors in CdS," Physica B **273–274**, 907–910 (1999).
18. D.-E. Arafah and R. Ahmad-Bitar, "Induced Defects and Structural Changes Resulting from the Processing of CdTe and CdS Thin Film," Sol. Energy Mat. Sol. Cells **64**, 45–54 (2000).
19. I. D. Desnica-Frankovic, U. V. Desnica, A. Stotzler, and M. Deicher, "Study of Microscopic Mechanisms of Electrical Compensation of Donors in CdS by Fast Diffusors (Cu, Ag, Au)," Physica B **273–274**, 887–890 (1999).