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STACKING DISORDER OF ZINC SULFIDE CRYSTALS FROM BLACK SMOKER CHIMNEYS (MANUS BACK–ARC BASIN, PAPUA–NEW GUINEA REGION)

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Hexagonal ZnS platelets and prisms (up to 1 mm in size) from black smoker chimneys of hydrothermal field of Manus back-arc basin (Papua-New Guinea) were studied using a set of methods (ore microscopy, SEM, electron microprobe analysis, X-ray and electron diffraction, and HRTEM). The most prominent isomorphic admixture is Fe (6.6 — 9.6 mol.% in the ZnS structure). Both X-ray and electron diffraction patterns and HRTEM images have shown that ZnS-crystals despite of their hexagonal habitus contain three different modifications in nanoscale: polytypes 3C and 2H and defect phase with alternating layer- stacking. This fact is a result of nonequilibrium growth conditions.
2 tables, 6 figures, 34 references.

Zinc sulfide in nature mainly occurs as cubic sphalerite (3C) and hexagonal wurtzite (2H)[1] though among synthetic products more than 190 ZnS polytypes are known, the most of which is formed from the gas phase (Mardix, 1986).

Synthetic ZnS crystals are of large interest being important semi-conductors. Structural stacking disorder, twinning, intergrowths, dislocations in synthetic ZnS crystals were in detail discussed in many papers and some studies are conducted with use of high-resolution electronic microscopy (HRTEM) (Qin *et al.*, 1986; Mizera, Sundberg, 1986; Strock, Brophy, 1996, etc.). The disordered distribution of different polytypes (3C, 2H, 4H, 9R, etc.) was also described in natural ZnS crystals from different continental deposits (Fleet, 1975, 1977; Akizuki, 1981; Pósfai *et al.*, 1988; Vergilov *et al.*, 1992, etc.). However, there are problems in understanding the reasons of such defective microscopic structures in ZnS till now. Studies of zinc sulfides from modern oceanic hydrothermal formations can help to get additional data regarding this problem.

A characteristic feature of ocean hydrothermal mounds formed at a depths of more than one kilometer is the presence of sulfide chimneys, from a «pencil» size of some centimeters to thick columns raising to the height of 2—3 storey building (to 10 m and more). Chimneys grow in hot fluids (300 — 400° C) discharge places at the front of their mixing with cold (about 2° C) sea water. An outflow velocity of fluids is usually very high (up to 15 m/s in the Mid-Atlantic Ridge). In outflow places, lifting fluids in the active phase form extensive plumes of smoke in sea water (from here their name — «smokers»), presented by very fine mineral suspension, in quantities dispersing in ocean water.

Sulfides of the system Cu-Fe-Zn-S form the mineral base of ocean ores. Among zinc sulfides, sphalerite is the main mineral of underwater mounds, but wurtzite, which is not common in continental deposits, is frequently registered also. This is one of features of ocean ores (Mozgova, 1999, 2001, 2002; Mozgova, 2002). It is necessary to emphasize that in most cases wurtzite, because of very fine segregations, is diagnosed in underwater ore by the hexagonal form of crystals.

The purpose of this work is to give a detailed characteristic of hexagonal ZnS crystals from modern ocean sulfide ores from the Manus basin.

Geological position

Back-arc spreading centre of the Manus basin is within the axial volcanic arch «Red Star» of the internal rift about 2 km in width, characterized by extremely high spreading speed (up to 12 cm/year). Hydrothermal deposits form on pillow basalts at a depth of about 2500 m being represented by numerous chimneys from 1 m to 4 m in height (the main tower attains 14 m). Socle parts of chimneys are composed of ore crusts mainly consisting of barite

[1] Matraite, the third ZnS polymorph (R3m), named after the unique place of find, is indicated as an independent species — hexagonal (Anthony *et al.*, 1990), trigonal (Blackburn *et al.*, 1997), rhombic (Vaughan, Craig, 1978) or as trigonal wurtzite (Minerals, 1960)

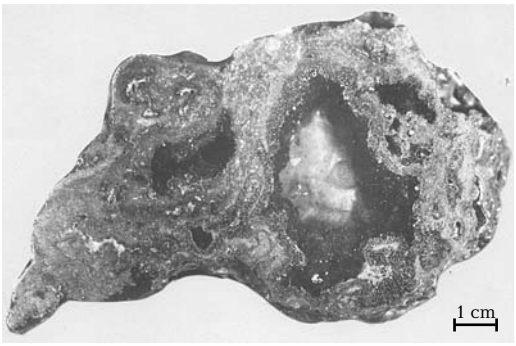


FIG. 1. Polished section of specimen № 2255-15A from an inactive chimney. Sulfides (mainly ZnS) have a zonal arrangement around the channels. The channels were cemented with epoxy resin before polishing. White irregular inclusions and fine zones are anhydrite and partly opal

and opal with disseminated impregnation of sulfides (Bogdanov, Sagalevich, 2002). Samples for studies were received from the Shirshov Oceanological Institute of the Russian Academy of Sciences. They have been collected in 21st cruise of the scientific vessel «Academician Mstislav Keldysh» in 1990 (Lisitsyn *et al.*, 1992).

Methods of studies

The morphology of revealed ZnS crystals was studied using two scanning electronic microscopes — JEOL JSM-T20 and Hitachi S-800. Structural relations between zinc sulfides and other minerals (sample №2255-15A) were observed under microscope in reflected light. Polished sections were made without heating.

The chemical composition was studied by X-ray microanalyser MS-46 «CAMECA» under the following conditions: accelerating voltage 20 kV, probe current 20 – 40 nA, standards (analytical lines) — ZnS (ZnKα and SKα), FeAsS (FeKα), $CuFeS_2$ (CuKα), CdSe (CdLα) and pure metals Mn and Ag (MnKα and AgLα).

X-ray diffraction characteristics were received in Guinier camera (Cu-radiation, internal standard — Si) and Laue and Weissenberg singlecrystal cameras. Electronic diffraction was studied in microscopes JEOL JEM 100CX (IGEM) and JEOL JEM 200CX (Arrenius Laboratory). The same material was used to receive a diffraction pattern (GIN of the Russian Academy of Sciences).

For studies under electronic microscope, selected ZnS grains were pulverized in an agate mortar in presence of *n*-butanol and then a drop of suspension was put on a copper grid. HRTEM images were received in electronic microscope JEOL JEM 200CX, equipped with the goniometric device (inclination ±10°), at operating voltage of 200 kV.

Sample description

We have studied a polished cross section of an inactive chimney 8 cm long and about 6 cm wide, with abundant pores and irregular-shaped channels, from 1 – 3 mm up to 3 cm in size (Fig. 1). Most of channels are empty, some are filled in with anhydrite. Fine-grained aggregates of sulfides, mainly zinc sulfides, surround large channels, repeating their outlines. Zonality is notable in distribution of sulfides around of channels, basically due to alternation of thin zones of non-metal minerals (anhydrite and subordinated quantities of opal).

Walls of channels are covered with crusts of microdruses consisting of well crystallized fine ZnS crystals with mirror faces — hexagonal prisms up to 30 microns in height and to 20 microns wide (Fig. 2a) and hexagonal platelets up to 60 microns in diameter (Fig. 2b). It is necessary to emphasize that prisms also show a subparallel transverse structure. Fine chalcopyrite tetrahedrons are notable on faces of lamellar crystals. The base of microdruses consists of cone-shaped and columnar aggregates of transverse subparallel platelets (Fig. 2c, d). They make walls of channels. In transverse sections it is visible that size of platelets in cone-shaped aggregates increases towards the channel and thus the aggregate in this direction extends. Similar morphology of hexagonal wurtzite crystals was described in earlier publications (Oudin, 1983; Rö sch, Marchig, 1991). The conic form of aggregates and their lamellar structure are well manifested in polished sections in reflected light, and there are numerous chalcopyrite grains basically located near edges of ZnS aggregates (Fig. 3). Columnar aggregates voutward from the channel are usually changed by assemblaes of irregular grains of the same sulfides cemented by anhydrite and opal.

Prismatic and lamellar ZnS crystals in microdruses have light brown color, columnar aggregates are dark brown with a greenish tone. Both varieties of ZnS in polished sections have in reflected light usual gray color and strong reddish-brown internal reflexes. Despite of hexagonal shape of crystals, the anisotropy is not noted in them.

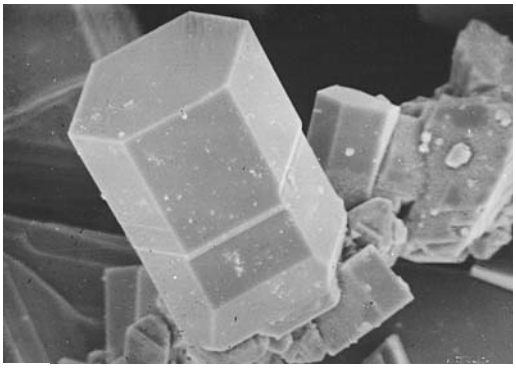
X–ray microanalysis

Chemical composition was determined in polished sections of five ZnS crystals. Pre-

Table 1. Electrron microprobe data of zinc sulfides from Manus (Sample № 2255-5A)

		Contents, mass. %								
Grain	*Anal*	*Zn*	*Fe*	*Cu*	*Mn*	*Ag*	*Cd*	*S*	*Total*	*Formula*
I*	1	62,68	3,83	0,05	0,08	0,02	0,00	32,63	99,29	$(Zn_{0,94}Fe_{0,07})_{1,01}S_{0,99}$
	2	61,42	3,96	0,04	0,07	0,04	0,00	32,90	98,43	$(Zn_{0,92}Fe_{0,07})_{0,99}S_{1,01}$
	3	62,00	3,75	0,05	0,06	0,04	0,00	32,37	98,27	$(Zn_{0,94}Fe_{0,07})_{1,01}S_{1,00}$
II*	4	61,07	5,28	0,12	0,09	0,04	0,00	32,54	99,14	$(Zn_{0,91}Fe0,09)_{1,00}S_{0,99}$
	5	61,98	4,46	0,12	0,08	0,04	0,00	32,56	99,24	$(Zn_{0,93}Fe_{0,08})_{1,01}S_{0,99}$
	6	60,80	5,42	0,11	0,11	0,05	0,00	32,53	99,02	$(Zn_{0,91}Fe_{0,10})_{1,01}S_{0,99}$
	7	61,67	4,77	0,09	0,08	0,04	0,00	32,77	99,42	$(Zn_{0,92}Fe_{0,08})_{1,00}S_{1,00}$
III**	8	61,01	5,22	0,13	0,12	0,00	0,11	30,67	97,31	$(Zn_{0,94}Fe_{0,10})_{1,04}S_{0,.96}$
	9	61,76	5,28	0,13	0,12	0,00	0,11	31,13	98,53	$(Zn_{0,94}Fe_{0,09})_{1,03}S_{0,96}$
IV**	10	62,04	3,83	0,06	0,08	0,00	0,00	33,30	99,31	$(Zn_{0,92}Fe_{0,07})_{0,99}S_{1,01}$
V**	11	62,04	4,03	0,33	0,09	0,00	0,11	34,11	100,72	$(Zn_{0,91}Fe_{0,07})_{0,98}S_{1,02}$
	12	62,09	4,74	0,23	0,09	0,00	0,00	34,47	101,62	$(Zn_{0,90}Fe_{0,08})_{0,98}S_{1,02}$

*I and *II — two crystals previously investigated by X-ray monocrystal method. Analysis 1 — core of the crystal; analyses 2 and 3 — its peripheral part; analyses 4 — 7 from different points of the second crystal (Fig. 2a);
** III — V — ZnS crystals previously investigated under scanning electronic microscope. Analyses 8 — 9 — columnar aggregate of dark brown crystals with greenish tint, containing abundant fine inclusions of chalcopyrite (Fig. 2c); 10 — hexagonal platelet from microdruses; 11 — 12 — aggregate of dark brown irregular grains with chalcopyrite inclusions from the base of microdruses (Fig. 2d)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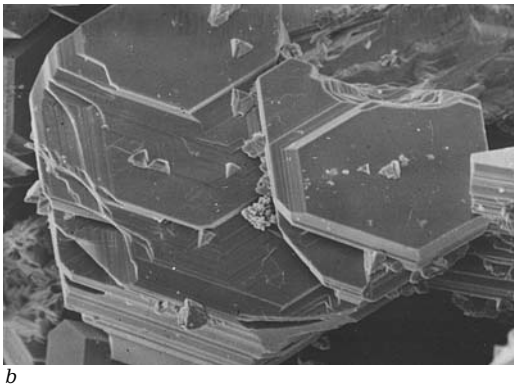
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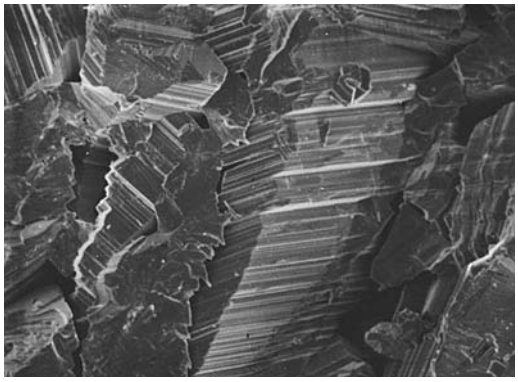
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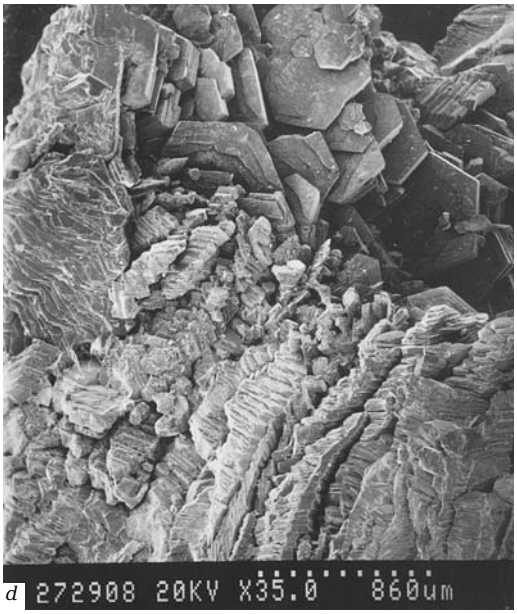

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FIG . 2. The morphology of ZnS crystals and their aggregates (scanning electron micrographs): a — regular hexagonal prism; b — aggregate of hexagonal platelet ZnS with small chalcopyrite tetrahedrons on their faces; c — columnar cone-shaped aggregates of platelet crystals; d — microdruses of hexagonal platelet ZnS on its columnar aggregates

Table 2. X-ray data of zinc sulfides from Manus in comparison with standard data of wurtzite (JCPDS 36-1450) and sphalerite (JCPDS 5-566)

		wurtzite JCPDS 36-1450			*sphalerite JCPDS 5-566*		
I	*d*	*I*	*d*	*(hkl)*	*I*	*d*	*(hkl)*
5	3,311	100	3,310	100			
10	3,131	84	3,129	002	100	3,123	111
4	2,934	87	2,926	101			
2	2,707				10	2,705	200
1	2,276	28	2,2734	102			
10	1,914	81	1,9103	110	51	1,912	220
1	1,766	54	1,7642	103			
2	1,657	11	1,6543	200			
10	1,633	47	1,6303	112	30	1,633	311
1	1,603	12	1,5994	201			
1	1,566	2	1,5641	004	2	1,561	222
1	1,251	6	1,2506	210			
1	1,240				9	1,240	331
1	1,229	9	1,2264	211			
1	1,213	2	1,2103	114	2	1,209	420

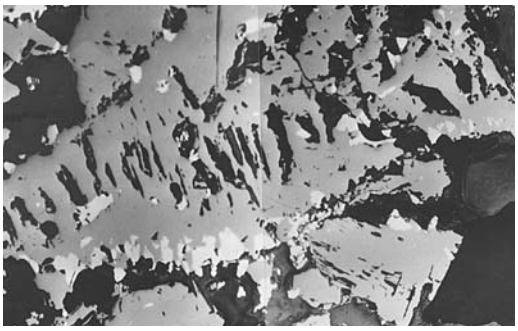


FIG . 3. Cone-shaped columnar ZnS aggregates in polished sections under the microscope in reflected light; the lamellar structure of the aggregate is emphasized by cross dark strips of polish defects (white grains — chalcopyrite, black, at the left — the channel)

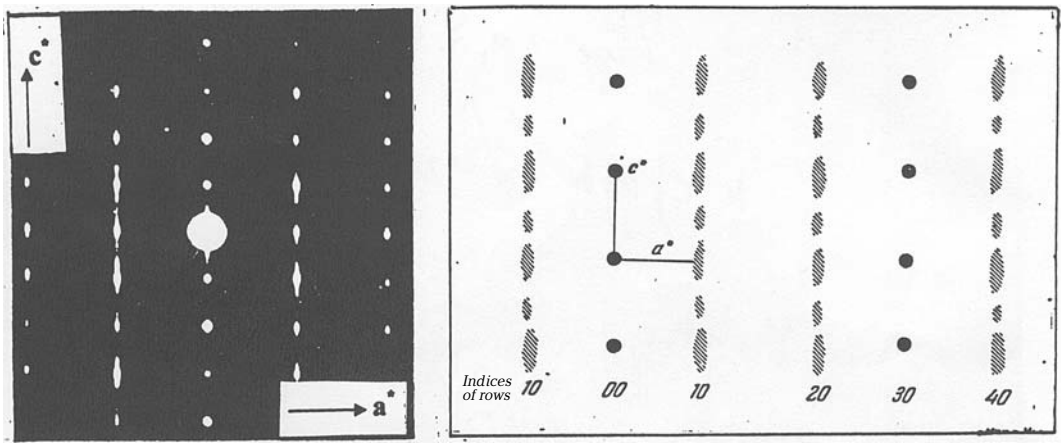
viously, two of them were investigated by a single crystal method of, other three, representing different zones — by a method of electron microscopy (Table 1). The results show that the basic isomorphic admixture in all investigated samples is iron, which contents vary between 3.75 and 5.42 mass.% corresponding to 6.6 – 9.6 mol.% FeS. This is much below values of similar ZnS grains from black smokers in East Pacific Rise — 20.1 mol.% FeS (Rö sch, Marching, 1991) and 21.4 – 32.8 mol.% FeS (Oudin, 1983). Variations of iron content within separate crystals and grains do not exceed 1 mass.%.

As seen from Table 1, ten from twelve calculated formulas show insignificant deviations from the stoichiometry — from 0.5 to 2 at. % for S, which agrees with known data on insignificant non-stoichiometry of ZnS (its total volume is about 1 at. %) (Scott, 1968; Scott, Barnes, 1972). In most cases (8 of 10) these deviations in our analyses are directed towards decrease of sulfur. Only two analyses of the darkest granular aggregates from the base of microdruses are characterized by some surplus of this element.

Total amount of other admixtures (Mn, Cu, Ag, Cd) is below 0.5 mass. %. The copper content in part is probably defined by pollution with chalcopyrite, especially in samples III and V, where especially abundant fine inclusions of this mineral are observed under ore microscope.

X-ray powder diffraction

X-ray diffraction pattern received in Guinier camera has shown clear reflections, which can be attributed to two ZnS isomorphs — 3C



a *b*

FIG. 4. Microdiffraction pattern (or SAED-selected area electro diffraction) from ZnS microcrystal along [010] and its interpretation: a — representative SAED ZnS pattern containing reflections from wurtzite and sphalerite; b — reciprocal lattice diagram of disorder ZnS-microcrystal according to A.Guinier (Guinier, 1961, page 463)

and 2H. Calculations of powder diffraction patterns of investigated samples are given in comparison to standards for wurtzite and sphalerite (Table 2). Most of lines overlap and cannot be used for diagnostic of polytype. At the same time, as seen from the table, the experimental roentgenogram shows two reflections (d = 3.311 and d = 2.934) close to intensive reflexes of wurtzite (d = 3.310 and d = 2.926) and a pair of lines (d = 2.707 and d = 1.240) characteristic of sphalerite (d = 2.705 and d = 1.240). This data indicate the presence of both polymorphs in investigated grains. Distribution of intensities in experimental data cannot be explained by a mechanical mixture of two phases as the intensities of corresponding lines do not correspond to the sum of intensities of two polymorphs.

Diffraction from single crystals

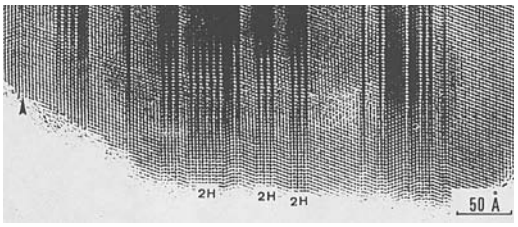
Fig. 4a shows microdiffraction results being a typical image of single crystal along [010]. Its comparison with the scheme (Fig. 4b) shows that both wurtzite and sphalerite are present in the volume of microcrystal. Diffused character of reflections on «layer» lines with index h = 1, 2 is an attribute of layer stacking mistakes of closely packed layers of sulfur atoms, and their elongation along axis c^*, including zero unit — an attribute of small thickness of alternating layers.

The x-ray data received in the Weissenberg camera (Fig. 5) shows zero scan *(h0l)* of one of chips representing the same plane of reciprocal lattice containing diffusion rods at the same h values as in the microdiffraction image (see Fig. 4).

High–resolution electronic microscopy

In images received by methods of high-resolution electronic microscopy (Fig. 6a-c) numerous mistakes of overlapping of closely packed ZnS layers are distinctly visible. At preparing specimens, the material is broken up in a water suspension by ultrasound along planes (100) and this gives a possibility to observe features of stacking disorder and their alternation along axis [001] in wurtzite. It relieves of necessity to prepare a specimen of certain orientation and thickness. In all images, the alternation of sphalerite and wurtzite fields as well as their mixed overlapping are shown. So, in Fig. 6a, plots of cubic stacking with thickness of about 50Å prevail, in Fig. 6b, hexagonal stacking prevails. The image 6c contains a plot of a crystal with the greatest concentration

FIG. 5. Single crystal XRD ZnS pattern (h0l) obtained in Weissenberg camera. Curved lines with 10l and 20l indexes contain diffusion rods in reciprocal space. It is a result of the staking faults



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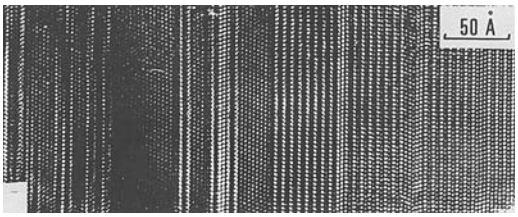

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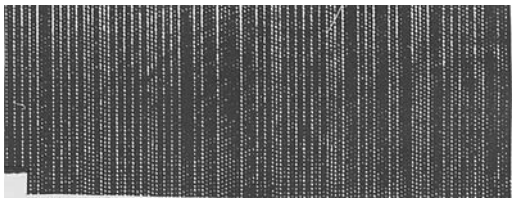

c

FIG . 6. HRTEM-image of some investigated microcrystals. Vertical white point rows are planes of closely packed atoms. Crystal sections with the slope rows are cubic stacking; crystal sections with two layers are hexagonal stacking: a — a part of crystal with dominant cubic stacking (wurtzite 2H stacking is indicated); b — a part of crystal with dominant hexagonal stacking; c — a part of crystal with mixture stacking (it is in this range of defect concentration that the calculation has been conducted)

of stacking disorder.

Interpretation of diffraction features and HRTEM–images

V.A. Drits with co-authors (1994, 1995, 2003) showed that the consecutive alternation of closely packed layers of zinc sulfides is subject to Markovian statistics, which supposes dependence of overlapping style of each subsequent layer on the arrangement of the previous layers, which results in some ordering. It means a possibility of diffraction from a substance, which can be considered, in condition of disorder presence, as intermediate between crystalline and amorphous. The method of calculation of similar layered materials was repeatedly described (Drits, Tshoubar, 1991, etc.).

For this object, the calculation was conducted under earlier described programs (Sakharov at al., 1982). As the use of HRTEM-images made it possible to calculate how many previous layers influence the position of the subsequent one, the value of short-range order factor equal to 2 was used in calculation (its value is usually determined by searching till reception of the best agreement with the experiment).

From a high volume of investigated material representing assemblage of described above crystals, a diffraction pattern has been received. Theoretical calculation of intensities pattern lines in the field of angles 2θ with maximum intensities of reflections for each of three phases — wurtzite, sphalerite and mixed phase — was conducted. Comparison of experiment with theoretical mixtures with various quantitative ratios of components has allowed to establish that the ratio of 14:17:69 best corresponds to the experiment. The sequence of figures corresponds to sphalerite, wurtzite and defective ZnS indicating a prevalence of the most unorganized material in the sample.

Discussion

Wurtzite is traditionally considered a high-temperature polymorphic modification of ZnS. According to D.Vaughan and J. Craig (1980), the stability field of wurtzite is above 1020° C. At the same time, on an example of wurtzite and other minerals, it has been convincingly shown, that «there are forcing factors due to which high-temperature forms are not only formed outside of stability fields, but also are preserved in a metastable state or a state of compelled equilibrium for a long time» (Urusov *et al.,* 1997, p. 57). One of essential factors of the compelled equilibrium is the phase dimensional effect representing «change of physical and chemical transformation parameters under effect of sizes of phases or other parameter related to the size, which is considered independent» (ibid., page 58). The action mechanism of this factor also was repeatedly illustrated on an example of zinc sulfides (Tauson, Chernyshev, 1981; Tauson, Abramovich, 1982, Urusov *et al.*, 1997, etc.). In addition, intergrain and interblock borders, structure defects, stabilizing action of admixtures, effect of sulfur activity, high hydrostatic pressure detaining increase of the surface of mineral phases, and other were registered as forcing factors. This concept helps to understand appearance of hexagonal and rhombohedral polytypes of ZnS in rather low-temperature deposits on continents (Vergilov *et al.*, 1992; Минеva-Stefanova, 1993, etc.) and a wide distribution of wurtzite in ocean hydrothermal ores, which temperature of formation does not exceed 400° C (Krasnov at al., 1992).

The study has shown that crystals of zinc sulfides from the Manus basin, despite of hexagonal shape, are represented by coexisting at nanolevel three polymorphs of zinc sulfides: finely intergrowing polytypes 3C and 2H and partly ordered defective phase. Considering mentioned above conditions of black smoker formation, the mechanism of formation of «mixed» structural states of zinc sulfides could be interpreted from the concept of compelled equilibrum (Urusov *et al.*, 1997). Crystals 2H occur first, as most themodynamically stable in microparticles (the forcing factor is a «developed surface of phases», Tauson, Abramovich, 1982). With growth of crystals, when they get out of dimensional interval of the phase dimensional effect influence, structural transformations into more stable in new conditions phase 3C begins. However, impact of other forcing factors (internal factors — structural admixtures and disorder — and external — high hydrostatic pressure and decrease of sulfur concentration with evolution of process) creates a new condition of compelled equilibrium, at which the formed mixed structures are preserved and true equilibrium with complete transformation of crystal structure into sphalerite is not reached.

According to V.L. Tauson and L.V. Chernyshev (1981), finely dispersed heterogeneous systems are favorable for microblock growth of crystals, when a crystal grows due to accretion of not separate atoms, but their blocks. As plumes-smokes of smokers belong to such systems, it is possible to assume that the lamellar

structure of hexagonal prisms described above can be explained by such a mechanism of growth.

Detected in the investigated samples of zinc sulfides insignificant deviations of Me/S ratio from ideal value agrees with the idea of non-stoichiometry of this compound (Scott, 1968; Scott, Barnes, 1972). The data indicated in quoted works characterize wurtzite by some deficit of sulfur and respectively surplus of zinc, and sphalerite has opposite ratio of these elements. This allows to assume that variations of this ratio in Manus samples reflect variability of quantitative ratio of three various polymorphs of zinc sulfides, established within different investigated hexagonal ZnS crystals. It is necessary to note that, as all three polymorphs meet within one «monocrystal», the form of crystals in this case cannot be a sufficient diagnostic attribute for wurtzite and sphalerite. As noted above, at optical studies in polished sections under ore microscope this nanoheterogeneity is also not manifested. E. Oudin (1983) is probably right, describing morphologically similar crystals in ocean ores 21° N under the generic name «zinc sulfide».

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