UDC 549.283 : 548.51

NANOCRYSTALS OF NATIVE GOLD AND THEIR INTERGROWTHS

Margarita I. Novgorodova
Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, min@fmm.ru

Nanocrystals of native gold showing morphological similarity to their synthesized analogs were discovered as inclusions in quartz and sulfides. Nanocrystals tens of nanometers in size are of cubic, cubooctahedral crystalline and dodecahedral quasi-crystalline form. Numerous twins, absent in gold macrocrystals, including polysynthetic twins by (100), and penetration twins by cube were found, reducing the symmetry of the face-centered cubic structure of gold. 1 table, 11 figures, 23 references.

Nanocrystals, which are a special dimensional group (<0.1 micrometer across) in the class of finely dispersed gold, are rarely preserved in the mineralogenic processes. Being the initial form of growth of larger gold crystals, they can be detected among elements of a non-uniform, usually mosaic blocks or zonal, *gold particles*. Nanocrystals and their aggregates are preserved as inclusions in the mineral matrix. These are so-called *matrix*-stabilized nanocrystals preserved in unaltered ores during geological time in tens, hundreds, millions and billions of years, i.e. eternally from the experimenter's point of view.

The history of nanoparticle study — their morphology, properties, synthesis methods, including diverse composite materials used in modern industrial, technical and medical *nanotechnologies* — totals hundreds of publications. Natural nanoparticles of minerals are investigated insufficiently; published in one of the last issues of the Mineralogical Society of America review «Nanoparticles and the environment» (Nanoparticles ..., 2001) contains the data on structure of nanoparticles and their aggregates, phase transformations in nanoparticles, computer modeling of their properties and behaviour, magnetic characteristics of *nanomaterials* received at studies of synthesized *nanocomposites*. Few works on studies of nanoparticles of natural Fe, Ti, and Al oxides, Zn sulfides, and natural and technogenous nanoparticles in atmosphere are exclusions.

Special properties and in some cases unusual structures of nanoparticles are defined by thin equilibrium between surface energy and energy of crystal lattice in volume. At this, the dimensional effect is especially notable as with increase of particle size the share of surface atoms drops and the number of lattice cells of atoms in volume increases (Fig. 1). The dimensional effect is manifested in

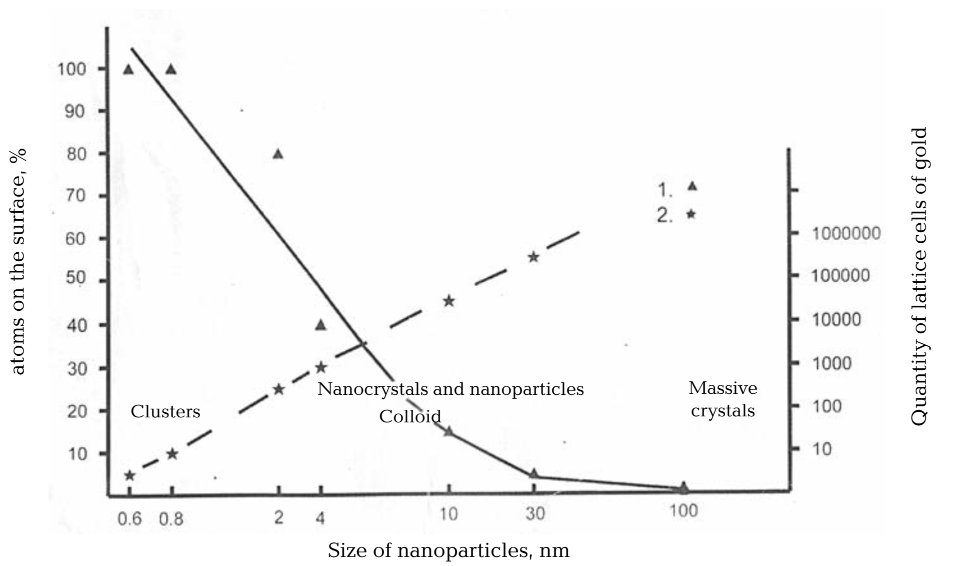


FIG. 1. Share (in %) of atoms on the surface and number of lattice cells in volume of gold nanocrystals depending on their size: 1 — atoms on the surface, %, 2 — quantity of lattice cells

Table 1. Concentration, sizes and form of particles of thin gold in sulfides

Deposit	*Sulfides*	*Au content, ppm*	*Size and form of sulfides grains*	*Size and form of gold particles*
Muruntau, Uzbekistan	Arsenopyrite	120-250	0,05-0,1 mm, rodlike crystals	0.07-0.1 micrometer, rounded inclusions
Bakyrchik, Kalba, Kazakhstan	Arsenopyrite	30-75	0,5-1 mm, prismatic crystals	2-25 micrometer, irregular particles
	Arsenopyrite	51-550	0,05-0,1 mm, rodlike crystals	0,1-1,5 micrometer , dendrites 0,01-0,1 micrometer , orounded particles
	Pyrite	2-32	0,3-1,2 mm cubic crystals	1-40 micrometer micrometer, wrong and flatted particles
	Pyrite	20-105	0,1-0,2 mm pentagon-dodecahedral crystals	0,5-1,5 micrometer rounded inclusions, microcrystals
Lebedinskoye, Central Aldan, Russia	Pyrite	2-125	0,4-1,0 mm cubic crystals	10-75 micrometer irregular and flatted particles
	Pyrite	5-220	0,1-0,2 mm octahedral holohedral and flatted crystals	1-10 micrometer, dendrites
	Pyrite	100-350	0,01-0,1 mm spheroids	0,1-1,0 micrometer, rounded particles

the morphology of nanoparticles and deviation of their structure from the structure of larger crystals. For metals with cubic face-centered cells, transition from the equilibrium cubooctahedral form of crystals to *quasicrystalline — icosahedral* and *dodecahedral — was established*. The *quasicrystalline* form of nanocrystals for the first time has been detected in gold, and later in other face-centered cubic metals.

Diffraction pattern of *icosahedral* and *dodecahedral* crystals of gold, in which structure translation of atoms are theoretically absent, are characterized by the presence of irrational and regular reflections from coherently connected domains, each of which has *face-centered cubic structure*. The domain structure is conditioned by the presence of twins — single or multiple, parallel or radial. The model of *icosahedron* and dodecahedron as multiple twins with *tetrahedral nucleus*, on face (111) of which five or twelve tetrahedrons consecutively growing for the first time was proposed by S. Ino in 1966 and later supplemented by a model of dodecahedron composed of multitwins by (100) (Ino, Ogawa, 1967). Ino (1969) has distinguished three types of twinned nanocrystals — with hexagonal cross-section (icosahedron composed of 12 tetrahedrons aggregated by (111); with pentagonal cross-section (dodecahedron composed of 5 tetrahedrons aggregated by (111); with rhomboid cross-section (dodecahedron of 5 tetrahedrons aggregated by (100)). The critical size of twinned nanocrystals is calculated as a function of such parameters as specific surface energy for planes (111) and (100), energy of twin borders, adhesive energy and density of elastic tension energy. Under calculations, limiting diameter of particles is 10.68 nanometers for Au and 7.56 nanometers for Ag; however, icosahedrons of gold with a diameter of 40 nanometers and dodecahedrons of silver with a diameter of about 300 nanometers were practically observed. The large multitwins grow due to introduction of dislocations reducing energy of elastic tension (Ino, 1969). In icosahedral particles, Schocli partial dislocations locate near surface, in dodecahedrons defects locate on twin borders (Marks, Smith, 1983). Theoretically, the stability of nanocrystals decreases in the series cubooctahedron > dodecahedron > icosahedron (Marks, 1984). The elementary tetrahedron (with four planes (111), considered as a nucleus in S. Ino's standard base model, is still less stable.

Decrease of energy saturation of synthesized nanoparticles and their ability to quick clustering is provided with formation of protective shells, most often as organic ligands (Martin *et al.*, 2000; Lee Penn, Banfield, 1998) or synthesis in stabilizing environments — sol-gel synthesis, settling on polymeric matrixes, etc. (Petrov, 1986; Pomogailo *et al.*, 2000).

It has been established in experiment that clusters (nanocrystals) of metals (Ag, etc.), precipitated on a flat basal surface of graphite are mobile and diffuse with formation of films, which growth stops when mobile clusters achieve the size of 14 nanometers; the diffusion is hindered at steps of matrix plane growth (Caroll *et al.*, 1997). Collective movement of many thousands of atoms incorporated in nanoparticles of crystal structure is stated in many works (Gao *et al.*, 1987; Thurn-Albrecht *et al.*, 1999).

In the nature, matrix-stabilized nanoparticles of native gold precipitate from hydrothermal solutions of inorganic salts on a mineral matrix, on which surface they stabilize in active points or in micropores. Natural sol-gel synthesis occurs at formation of ore in some epithermal deposits.

Despite of numerous publications regarding finely dispersed gold (Bürg, 1930;

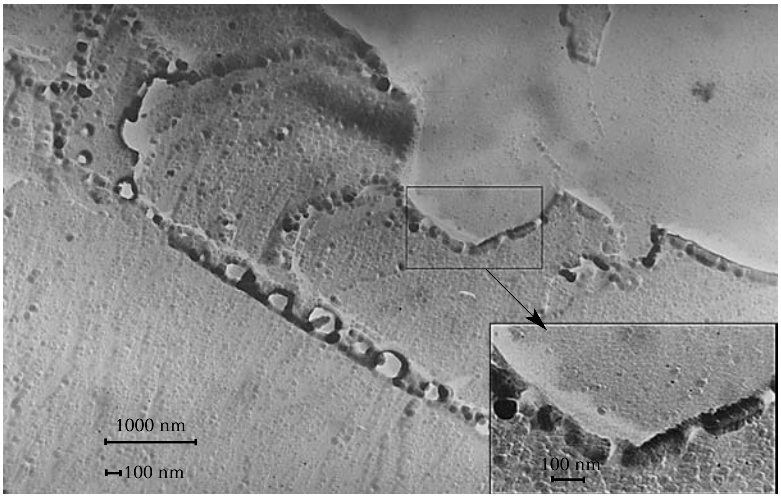


FIG. 2. Gold nanocrystals extracted on a replica (black) in a zonal arsenopyrite crystal in intergrowth with pyrite (light gray). Polished section etched by agua regia. Length of scales is 1000 and 100 nanometers. Bakyrchik deposit, Kalba

Haycock, 1937; Coleman, 1957; Schweigart, 1965; Hausen, Kerr, 1965; Peter, 1973, etc.), its most thin part — nanocrystals — is insufficiently investigated. The objective of this paper is to fill this gap to some extent on the example of nanoinclusions of gold in sulfides and quartz from gold-ore deposits of Siberia, Transbaikalian region, Far East and Central Asia.

Investigation Methods

The miniaturization of investment objects requires application of precision methods, the main of which for direct-viewing is the complex of analytical methods of electronic microscopy — scanning (SEM) and transmission (TEM) microscopy. We used transmission electronic microscopy with application of target cellulose-coal replicas from the chip surface of samples and polished sections. At such approach, a preliminary separation of thin class gold is not required; the sample preparation consists in examination of selected objects using light microscope and labeling of the necessary site for plating. For manufacturing of replicas, coal film was applied on samples in vacuum ionization-thermocouple gage VIT-3 at high vacuum. The received coal film (one-stage coal replica) was separated using gelatin solution, which solidification resulted in formation of two-step cellulose-coal replica. Particles of substance extracted on the film were investigated for determination of composition with the help of the energy-dispersion analysis and structure with the help of electron diffraction method.

Both fresh chips of samples and previously chemically or ionically etched surfaces were studied. As etching agents, acids HNO_3 for sulfides and aqua-regia — HNO_3 + HCl (1:3) — for native gold were used. The etching revealed the internal structure, borders of grains and disorder of studied crystal surfaces.

Experimental works on settling of gold nanoparticles from aqueous solution of gold chloride [$AuCl_4$] on sulfide substrate have been also carried out.

Gold Nanocrystals in Sulfides

Earlier, at study of finely dispersed gold in sulfides, direct dependence of gold concentration in

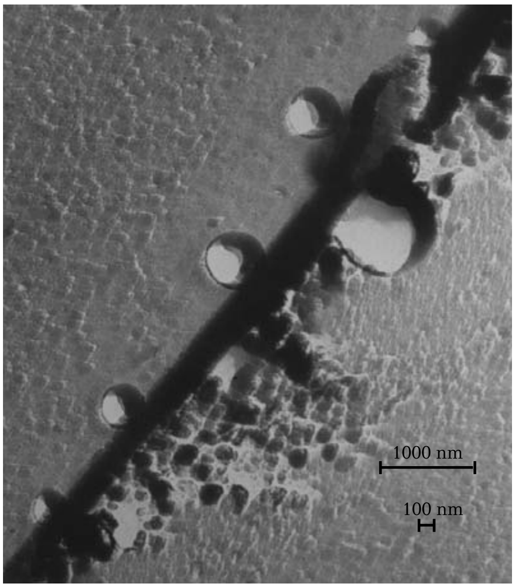


FIG. 3. Imprints of rounded gold dodecahedrons at a step of crystal growth in arsenopyrite. Polished section etched by agua regia. Length of scales is 1000 and 100 nanometers. Bakyrchik deposit, Kalba

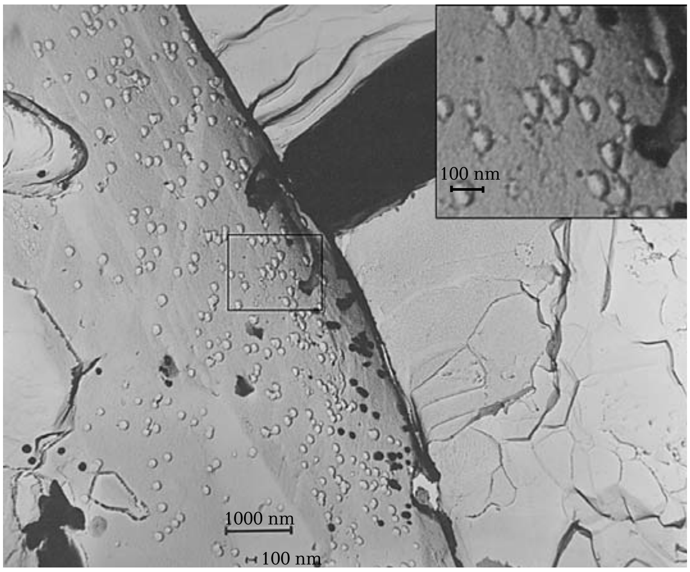
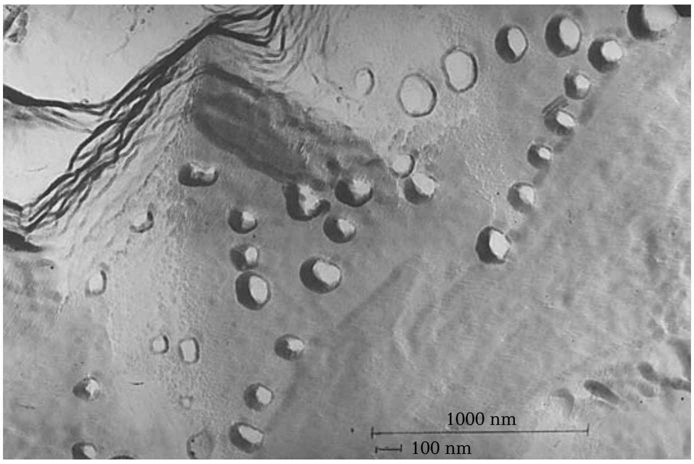
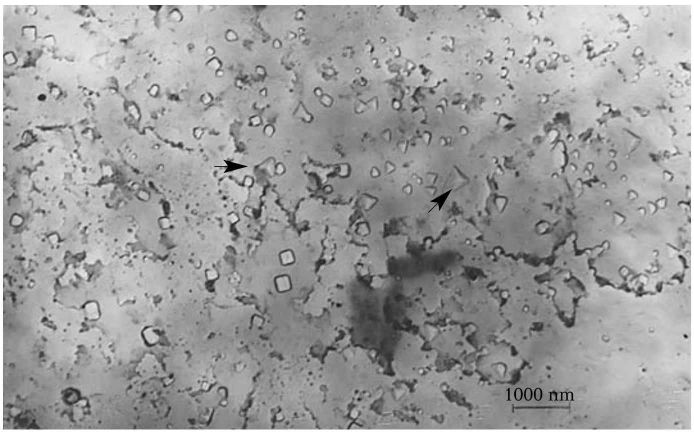


FIG. 4. Gold nanocrystals precipitated on a prism face of arsenopyrite crystal. Length of scale is 1000 nanometers; in box — 100 nanometers



a



b

FIG. 5. Gold nanocrystals in silicates: a — on sericite-quartz matrix; arrows show twin aggregates of tetrahedrons; length of scales is 1000 and 100 nanometers; b — on sericite-chlorite-quartz matrix, length of scales is 1000 and 100 nanometers. A chip of sample, without etching. Sovietskoye deposit, Yenisei Ridge

pyrite and arsenopyrite on sizes of sulfide grains, which also correlate with sizes of fine segregations gold particles (Table 1), has been shown. For arsenopyrite from the Bakyrchik deposit (Kalba), the highest concentration of fine gold particles along corrosion borders of relicts of early arsenopyrite (for which As/S ratio is <1) in late arsenopyrite with As/S ratio > 1 has been established (Novgorodova, 1994). Fine gold particles also settle on contacts of pyrite and arsenopyrite aggregates and along rectilinear steps of growth in sulfides.

Thin gold in zonal arsenopyrite for about 70 % consist of nanocrystals with sizes 50 to 100 nanometers, rarely up to 150 nanometers. Prevailing forms are cubes and cubooctahedrons; on pyrite/arsenopyrite contact chains of closely aggregated by (100) deformed cubooctahedrons occur, which form wire segregations with hexagonal end faces and ribbed extended surface (Fig. 2). Rounded segregations of gold 70—150 nanometers across, oriented in parallel to ternary articulation of pentagonal planes, occur on steps of growth in arsenopyrite. Morphology of such particles allows to attribute them to the ideal dodecahedron, i.e. to a quasicrystalline construction. Larger nanocrystals (> 250 nanometers) are represented by octahedrons with rounded edges (Fig. 3). The revealed inclusions of gold on zones of growth in pyrite are represented by cubooctahedrons, larger (> 200 nanometers) than nanoinclusions in arsenopyrite.

Artificially settled monodeispersed gold nanocrystals on the prism surfaces of a prismatic crystal of arsenopyrite are of similar sizes (~80 nanometers across). They are characterized by a little deformed, short by (111) form of cubooctahedron and the same orientation of ternary axis of nanocrystals. All gold nanocubooctahedrons grow together with arsenopyrite with face (111), forming interrupted chains

a

b

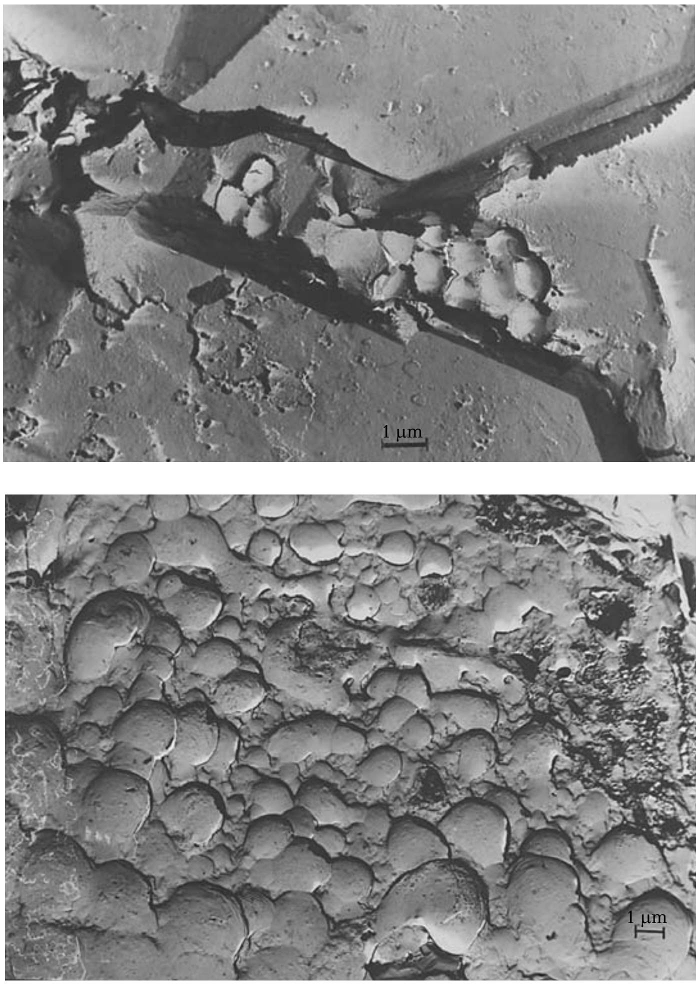


FIG. 6. Colloidal gold in quartz: a — in interstitial spaces of quartz microcrystals as closely packed aggregates of poorly poligonized globules; Taceevskoye deposit, Transbaikalian region; b — in aggregates of inequigranular globules. Sample chips without etching. The size of scale is 1 micrometer. Kualdy deposit, Uzbekistan

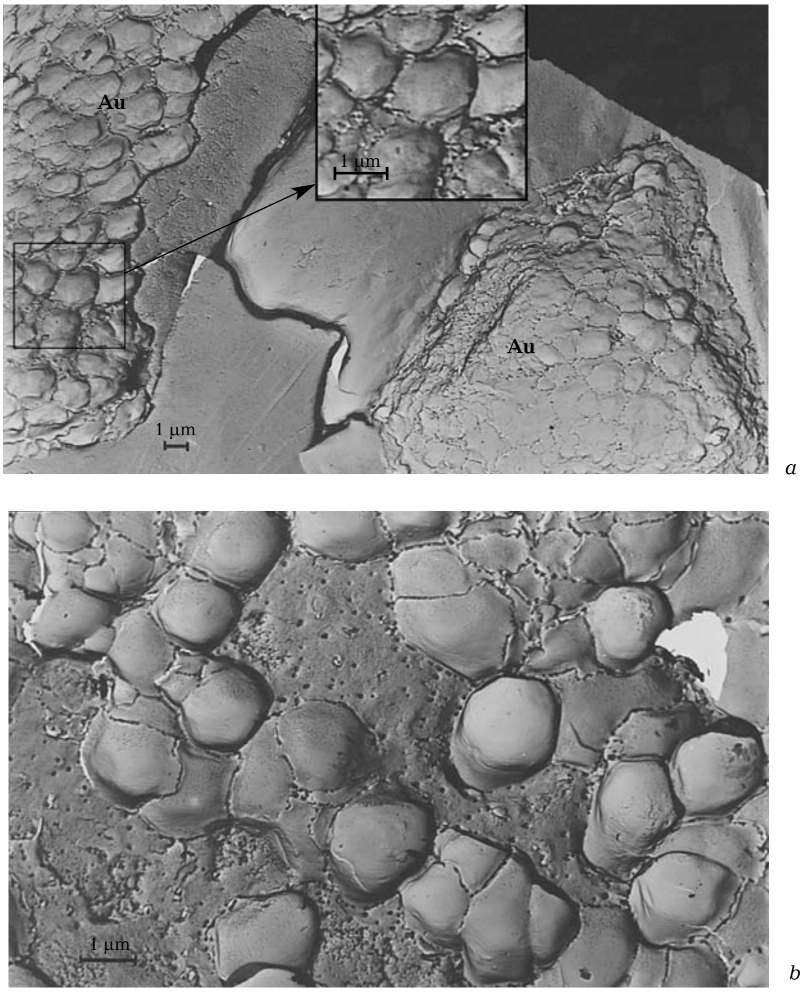


FIG. 7. Clots (a) and linear accumulations (b) of metacolloidal gold with syneresis cracks and detached polyhedral blocks in quartz. In box — blocks of dodecahedral shape. Sample chips etched with agua regia. Agatovskoye deposit, Kolyma. Length of scales is 1 micrometer

of close nanocrystals (Fig. 4). The greatest concentration of precipitated gold nanocrystals was established for the peripheral part of arsenopyrite grains.

Gold nanocrystals precipitated on the surface of cubic pyrite crystal are heterodispersed (60 – 90 nanometers across), have octahedral or cubooctahedral forms and have no orientation. Gold nanocrystals concentrate in the near-apical zone of cubic face of pyrite.

Gold Nanocrystals in Quartz and Silicates

Gold nanocrystals detected in relics of sericite-chlorite-quartz metasomatite in a gold-bearing quartz vein (Sovietskoye deposit, the Yenisei Ridge, Siberia) have sizes, close to those established for gold nanoinclusions in sulfides (10 to 100 nanometers). The nanocrystals are mainly cubic; however, extremely rare in gold nanotetrahedrons and their twins were also detected. Simple twins by (111) with penetrating angle (Fig. 5a), and more complex twins with rhomboid, pentagonal and hexagonal cross-sections supposing the multitwin nature of nanoparticles (Fig. 5b) are also present.

Much more complex crystal constructions of gold nanoparticles are characteristic of gold accumulations in fine festoons and thin-banded quartz streaks and veins from epithermal gold-silver deposits. Attributes of metacolloidal fabrics of such ores, established for many deposits of similar type (Petrovskaya, 1973), specify an original accumulation of colloidal substance in separate plots of ore deposition zones. It is shown that chalcedony-like quartz from thin-banded quartz veins, colored in yellowish tone, is saturated with

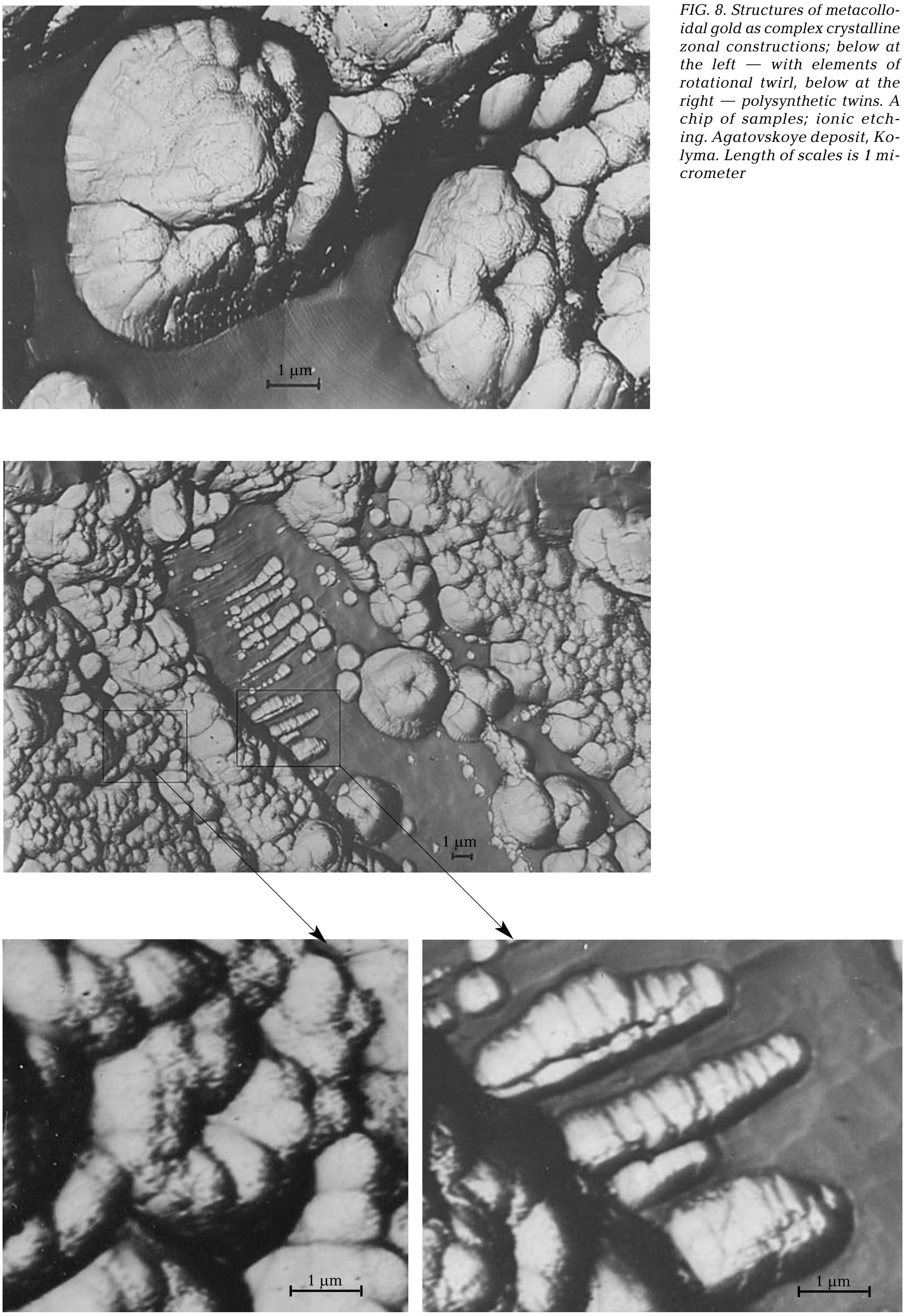


FIG. 8. Structures of metacolloidal gold as complex crystalline zonal constructions; below at the left — with elements of rotational twirl, below at the right — polysynthetic twins. A chip of samples; ionic etching. Agatovskoye deposit, Kolyma. Length of scales is 1 micrometer

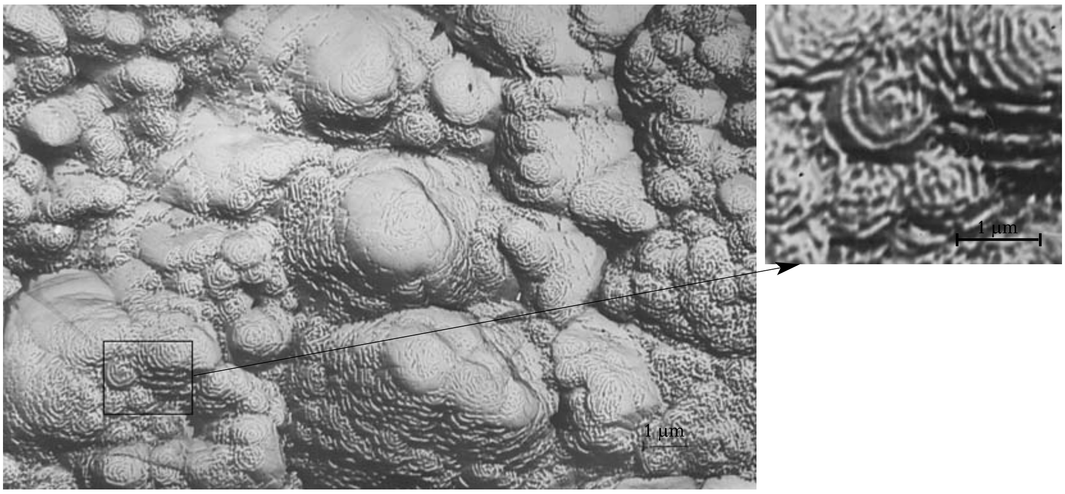


FIG. 9. Reniform aggregates of metacolloidal gold; right — a detail showing skeletal structure of fine blocks with an exit of screw dislocation at the centre. Sample chips; ionic etching. Agatovskoye deposit, Kolyma. Length of scales is 1 micrometer (left) and 100 nanometers (right)

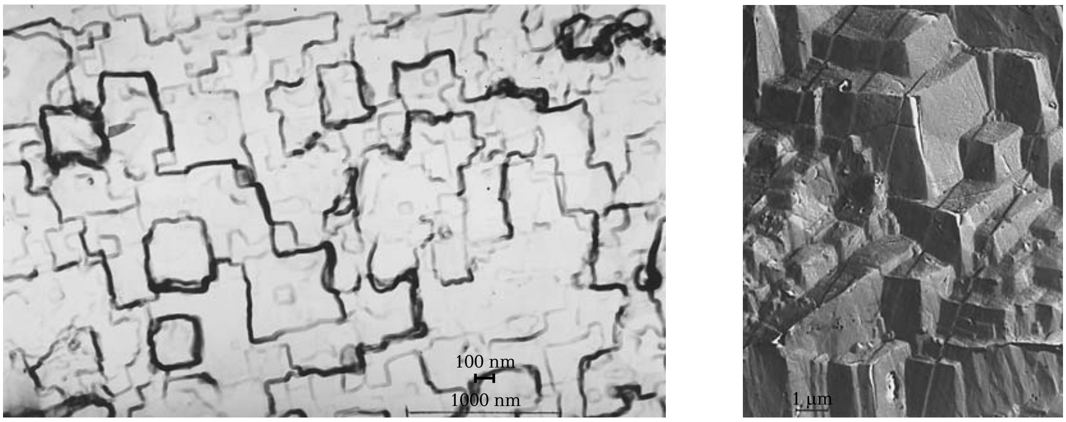
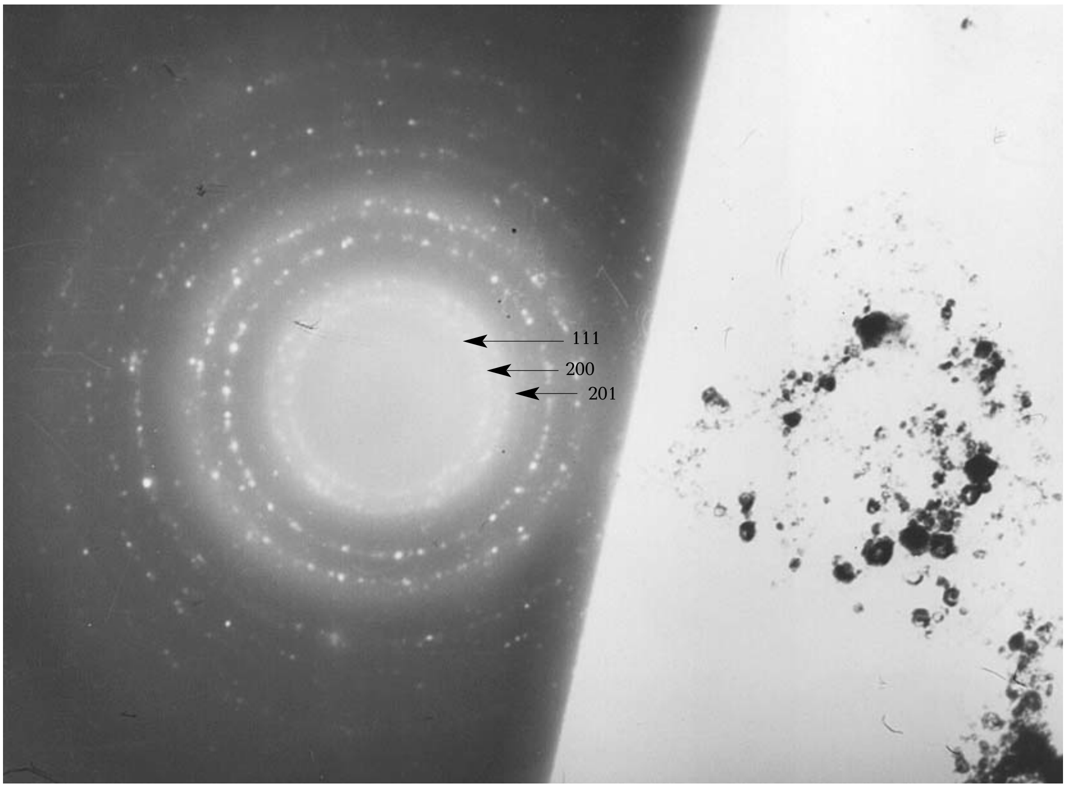


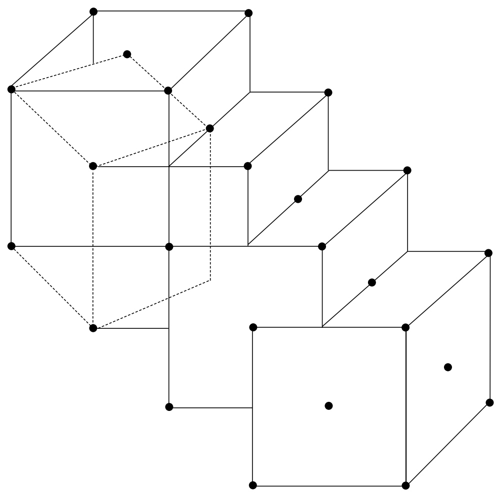
FIG. 10. Domain structure of plane (001) of flatted gold particle (a) and a step microrelief of a lateral border. Sample chips; ionic etching. Taseyevskoye deposit (Transbaikalian region). Length of scales is 1000 and 100 nanometers (left), and 1 micrometer (right)

so-called colloidal gold (Zhirnov, 1972). Colloidal gold includes linear and irregular accumulations of globular particles of 1 – 3 micrometers in size with smoothed or badly expressed polygonal outlines (Fig. 6). In some cases, a network of syneresis cracks with very thin pores on block contours detached as a result of coalescence can be seen on the surface of gold clots in chalcedony-like quartz after etching. Attributes of plastic flow (Fig. 7a) indicate that separation of blocks began before the complete solidification of colloidal substance. Chemical etching of gold globules reveals their polyhedral structure (Fig. 7b) and ionic etching — their complex internal structure (Fig. 8). Cross-sections of polyhedrons have hexagonal, rhomboidal or pentagonal form; the last is formed by intergrowths of fine blocks with formation of a general dodecahedral form (Fig. 7a). Blocks of a rounded form and zonal structure with an internal nucleus and an external shell (Fig. 8) also occur. The external shell and interblock substance consist of extended columnar individuals with reniform heads showing after etching a skeletal structure and attributes of spiral growth with the exit of screw dislocation at the centre (Fig. 9). The internal nucleus is non-uniform, it consists of closely aggregated subblocks with split apexes; subblocks grow together with rotational twirl along the vertical axis (Fig. 8).

The initial form of such complex skeletal crystals is a flatted cube complicated with faces {hk0} with high symbols, 15 – 20 nanometers thick, oriented by two most developed faces per-



a



b

pendicularly to the quartz matrix surface. In case of parallel intergrowth of flatted cubes, polysynthetic twins are formed, extended normally to composition plane and unknown in gold macrocrystals (Fig. 8). At a shift of intergrowth planes by S plane (010), twins of interpenetration by cube are formed. If such regular intergrowths aggregate with formation of flat gold particle, their traces are seen in the domain structure of plane (001) of gold particles or in unusual microrelief in steps of lateral chips (Fig. 10).

Electron Diffraction Images of Gold Nanoparticles

Similar subparallel orientation of polyhedral blocks in metacolloidal aggregates of gold calls attention. It is possible that orienting effect is rendered by the superstructure of the initial precipitated on quartz layer of colloidal gold. Experimental works (Connoly *et al.*, 1998; Martin *et al.*, 2000) show a tendency of metal nanoparticles, including gold, to collective self-organizing in closely packed cubic or hexagonal monolayers with the distal order. The parameter of such superstructure built not of separate atoms, but of their ensembles —

FIG. 11. Discrete-ring image of electron diffraction (a) and the scheme of tetragonal cell in interpenetration twins by cube in gold nanocrystals

nanoparticles — is determined, for example, for Ag as 81 Å (interplane distance d_{111}) (Connoly *et al.*, 1998), and for Au ~60 Å (distance between centers of nanoparticles with the size of 2 nanometers) (Martin *et al.*, 2000). These authors state that the superstructure is also preserved and volumetric 3D nanocrystals with the maximum size in some micrometers.

Crystallographically formed matrix-stabilized gold nanocrystals give both dot and discrete-ring images of microdiffraction with irrational reflections (111), inherent to multitwinned nanoparticles. The detailed consideration of such microdiffraction images is the theme for a separate paper, which is being prepared for publishing. The discrete-ring image of electron diffraction taken from cubic and cubooctahedral gold nanoparticles shows an additional reflection (201) (1.72 Å) indicating tetragonalization of face-centered cubic structures of gold. The decrease of symmetry is probably conditioned by ineterpenetration twins by cube, as shown in Fig. 11.

Conclusion

First discovered in nature matrix-stabilized nanocrystals of native gold in sulfides and quartz show morphological similarity to their synthesized analogs, differing by one order bigger sizes (tens of nanometers). They are cubic and cubooctahedral nanocrystals and dodecahedral quasicrystals, which are multitwin aggregates.

Unknown in gold macrocrystals polysynthetic twins by (100) and interpenetration twins by cube were detected, which reduce the symmetry of face-centered cubic structure of gold,

The author is sincerely grateful to K.E. Frolova, in teamwork with which the electron-microscopic images of gold have been received. This work was executed due to the assistance of the Basic Researches Program of the Russian Academy of Sciences, the State Contract # 10002-251/ONZ-04/182-188/160703-1081

References

Zhirnov A.M. Gipogennoe kolloidnoe zoloto v zolotorudnom mestorozhdenii Kauldy (Srednyaya Aziya) (Hypogene colloidal gold in the Kauldy gold-ore deposit (Central Asia) // Uzb. geol. zhurn. **1972**. # 1 (Rus.)

Petrov Yu.I. Klastery i malye chastitsy (Clusters and small particles) // M. Nauka. **1986** (Rus.)

Petrovskaya N.V. Samorodnoe zoloto (Native gold)// M.Nauka. **1973**. 347 p. (Rus.)

Pomogailo A.D., Rosenberg A.S., and Uflyand I.E. Nanochastitsy metallov v polimerakh (nanoparticles of metals in polymers). M.: Khimiya. **2000** (Rus.)

Burg G. Natur des Piriten nicht sichtbar enthalten goldes // Z. prakt. Geol. **1935**. Bd 43. H2.

Carrol S.J., Sceger K., Palmer R.E. Trapping of size-selected Ag clusters at surface step // Appl. Phys. Lett. **1998**. V. 72. N 3

Coleman I.C. Mineralogy of the Giant Yellow Knife gold mine // Econ. Geol. **1957**. V.52. N 4

Connoly S., Fullam S., Korgel B., Fitzmaurice D. Time-resolved small-angle X-ray scattering studies of nanocrystal superlattice self-aggregate // J.Am. Chem. Soc. **1998**.120. P. 2969–2970

Gao P., Gletter H. High resolution electron microscope observation of small gold crystals // Acta metal. **1987**. V. 35, N 7, P. 1571–1575

Hansen D.M., Kerr P.F. Fine gold occurrence at Carlin, Nevada // Ore deposits of the United States, **1933–1967**. N.Y. 1968

Haycock M.H. The role of the microscope in the study of gold ores // Canad. Min. a Metall. Bull. **1937**, V. 40, N 504

Ino Sh., Ogawa Sh. Multiply twinned particles at earlier stages of gold film formation on alkalihalide crystals // Journ. Phys. Soc. Japan. **1967**. V. 22. N 6. P 1365–1374

Ino Sh. Stability of multiply — twinned particles // Journ. Phys. Soc. Japan. **1969**

Lee Penn R., Banfield J.F. Imperfect oriented attachment: dislocation generation in defect-free nanocrystals // Science. 1998. V. 281. P. 969–971

Marks L.D., Smith D.J. HREM and STEM of defects in multiply-twinned particles // Journ. Microscopy. **1983**. V. 130, p. 2, P. 249–261

Marks L.D. Surface structure and energetics of multiplay twinned particles // Phil. Mag. **1984.** V. 49, N 1, p. 81–93

Martin J.E., Wilcoxon J.P., Odinek J., Provencio P. Control of the interparticles spacing in gold nanoparticles superlattices // J.Phys. Chem. B. **2000**, V. 104, N 40, p. 9475–9486

Nanoparticles and the Environment // Ed. J.F.Banfield, A.Navrotsky // Rev. Miner. A geochem. **2001**. V. 44

Novgorodova M.I. Finely dispersed gold from gold deposits of various genetic types // Process mineralogy XII. **1994**. TMS. P. 119–130

Schweigart H. Solid solutions of gold in sulfides // Econ. Geol. **1965**. V. 60. N 7

Turn-Albrecht T., Meier G., Mü ller-Buschbaum P., Patkowski A., Steffen W., Grü bel G., Abernathy D.L., Diat O., Winter M., Koch M.G.,