Native silver and its new structural modifications

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Native silver is distributed in ores of deposits of various genetic types, particularly gold-silver deposits. Examples of the latter are known in Central Asia and in Northeast USSR, within the Carpathian-Balkan region, in the western part of the American Cordillera, and in Japan. Judging from the available geological information, gold-silver deposits belong to shallow formations and are closely associated with products of volcanic activity, located in volcanic rocks of similar age of the andesite-dacite series, often within the vent facies of paleovolcanic structures of central type, or in direct proximity to subvolcanic dikes, concluding the volcanic cycle of development of the region. Ore deposits of this type differ in complex mineralogical composition, lengthy single-stage process of formation of the mineralogical association, often by telescoping and coincidence within the ores of various types of mineralization. The mineralogy of gold-silver ores of Northeast USSR has been described in papers by N. A. Shilo, M. S. Sakharova, V. I. Goncharov, A. S. Siderov, I. S. Rayevskaya, N. Z. Sav, A. N. Nekrasova, and others. Native silver, however, one of the principal economic minerals of these deposits, has been studied insufficiently.

Despite the similar crystal structures of gold, silver, and copper, the similar sizes of their atoms with similar structure of their electronic shells, complete miscibility in the series Au-Ag and Cu-Ag is not attained. A break of solubility in the high-silver part of the system Au-Ag, predicted by Vernadskiy (1904), was recently found by mineralogical (Petrovskaya et al., 1978) and experimental (Sakharova et al., 1976) work. The causes of the limited (1-2%) solubility of gold in silver are still not entirely clear. Also unclear are the causes of the extremely low mutual solubility of silver and copper, attaining in all (for 200°) 0.06% Cu on the one hand, and 0.83% Ag on the other (Kornilov et al., 1966). Native silver, as well as native gold and copper, has always been the standard face-centered cubic cell with space group Fm3m. Along with this there is known an antimonian variety of native silver, crystallizing in the hexagonal system — allargentum of Ramdohr (1962). The structure of allargentum, containing 8-15% Sb and observed together with dyscrasite as a product of the decomposition of a solid solution of silver and antimony, can be determined, according to Ramdohr, as a solid solution of silver in hexagonal closest packing with statistical distribution of antimony. Allargentum is generally accepted as a separate phase of the system Ag-Sb. This is not certain, however, and it is possible to assume that antimony is a stabilizer of the hexagonal structure characteristic of native silver. It thus becomes evident that careful studies are required of the structure of native silver, starting with the assumption that it can deviate from the face-centered cubic motif of the distribution of atoms.

METHODS OF WORK

Structural studies were carried out by the X-ray (Debye) and microdiffraction methods. Electron-microscope studies were made on the JEM-100S apparatus at the Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry of the USSR Academy of Sciences; some of the photographs were taken by L. M. Ol'shanskiy on the megavolt electron microscope JEM-1000 in the Baykov Institute of Metallurgy. Samples for study by transmission electron microscope were prepared by means of ion thinning by P. P. Perstnev in the Institute of Crystallography of the USSR Academy of Sciences. Thinning of the platy deposits of native silver was carried out by means of the ion beam in an atmosphere of argon in the Edwards JBJ-200 apparatus. The angle between the ion beam and the specimen surface was 20°, the impressed voltage 5 kV, the current of each beam 40 μa, speed of thinning 5 microns/hour. In the final stages of the thinning, after the first appearance of perforations in the sample, the surface was polished with speed of thinning 0.5 microns/hour and with a change of the angle between the beam and the surface of the sample to 7°.

The composition of the native silver was estimated by means of a microprobe attachment to the electron microscope JEM-100C of the "Kevex-Rays" (energy dispersive spectrometer). Quantitative analysis was made by A. I.

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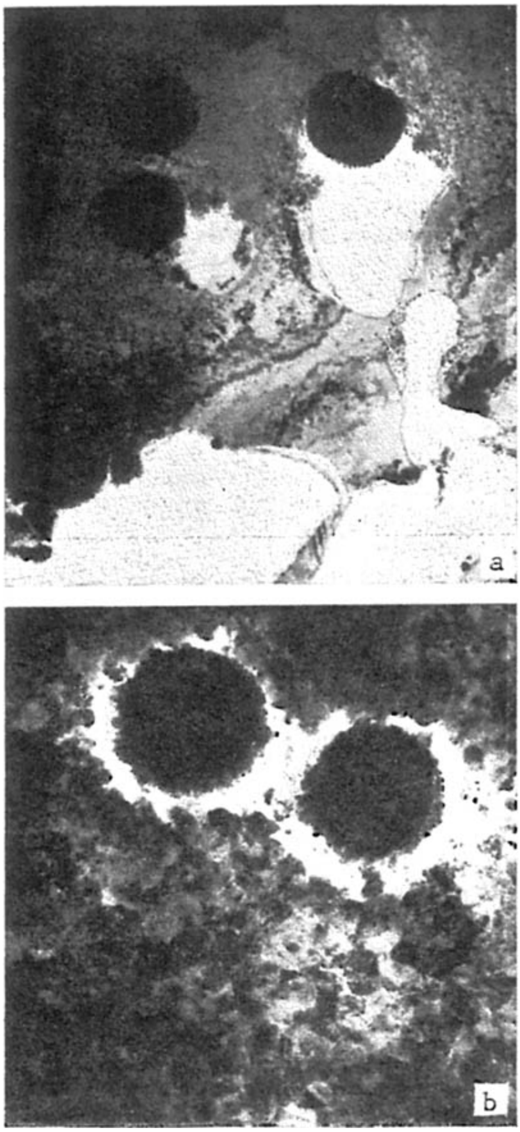

FIGURE 1. Globular deposits of finely acicular argentite in monocrystalline (a) and polycrystalline (b) areas of platy native silver. Electron microscope photographs of thinned preparations. Magnification: a - x 40,000; b - x 100,000.

Tsepin by the X-ray spectrographic method on the MS-46 microanalyzer of the "Cameca" firm.

MINERAL ASSOCIATIONS OF NATIVE SILVER

In gold-silver deposits of the type considered, the silver-containing mineral associations were formed in the late stage of mineral formation. In addition to native silver, often with inclusions of kustelite and electrum, they contain argentite, pyrargyrite, a late generation of pyrite, chalcopyrite, galena, tetrahedrite-tennantite, and many rare sulfosalts of Ag and Sb, sometimes Bi (sternbergite, polybasite, andorite, matildite, and aramayoite). Fine disseminations of native silver, with accompanying silver-containing minerals, are present both in ore veins of upper horizons with collomorphic-scalloped structure of quartz-adularia-chlorite aggregates, and in massive coarse-grained quartz-feldspar-rhodonite veins of lower horizons.

Constantly associated with native silver is a late generation of pyrite, chalcopyrite, galena, and tetrahedrite-tennantite, distinguished by high contents of admixed silver and often forming close, subgraphic, regular intergrowths with deposits of silver. These minerals evidently determine a narrow paragenetic association of native silver. Judging from the character of its interrelations with the accompanying argentite and silver sulfosalts, the latter belong to a somewhat later formation. Signs of corrosion and replacement of native silver by sulfur compounds are particularly clearly observed in its intergrowths with argentite. Relicts of native silver amid argentite occur in nearly all of the samples. Even where native silver forms isolated deposits in inclusions in the mineral silicate matrix, within each grain are found very small inclusions of argentite of unusual forms, suggesting their origin as the result of the process of sulfidization of native silver. These inclusions, a few tenths of a micron in size, have a regular globular and radiating-fibrous structure; individual fibers of argentite are a few hundredths of an angstrom wide (fig. 1). According to analysis on the "Kevex-Ray" microanalyzer, a small amount of copper is present in the argentite.

The close association between native silver and argentite thus bears a donor-acceptor character, and in the terminology of Petrovskaya and co-authors (1978) the second considered mineral association of native silver can be referred to the orthogenetic type — a variety of narrow mineralogical assemblages of components not in mutual equilibrium.

MORPHOLOGY OF DEPOSITS OF NATIVE SILVER

Most deposits of native silver are small (hundredths and a few tenths of a millimeter), irregular clotted or flattened forms. In unusual cases we see large (1-1.5 cm) dendritic intergrowths of platy crystals of native silver, flattened on the octahedron. The dendritic intergrowths are located in cavities of exfoliation along fine banded collomorphic-scalloped aggregates of quartz-adularia-chlorite composition.

TABLE 1. Chemical composition of native silver according to X-ray spectrographic analyses.

Sample	Ag	Au	Sb	Bi	Cu	Fe	Cr	Ni	Total
DV-261	98.79	0.33	0.37	0.23	—	—	—	—	99.72
	99.12	0.16	0.32	0.18	—	—	—	—	99.78
DV-133	99.93	0.04	0.04	0.18	—	—	—	—	100.19
DV-260	99.69	0.11	0.24	0.26	—	—	—	—	100.30
DV-300	98.90	—	—	—	0.50	0.01	0.01	0.01	99.43
	98.21	—	—	—	0.42	0.01	0.01	0.01	98.63

Note. Analyst - A.I. Tsepin.

Deposits of native silver are single grains, or rarely consist of intergrowths of two to three grains. Rare rectangular zones of growth, oriented along [110] in the plane of the octahedron, alternate toward the periphery of the grain with fine scalloped-curved converging zones. The native silver from the rhodonite-quartz veins has fibrous structure. Some grains of native silver from the quartz-adularia-chlorite ore have a completely concentric-zoned structure of collomorphic type. Relicts of such structure have also been found by etching platy crystals from dendritic intergrowths. Areas with a finely dispersed phase preserved within a crystal of native silver were clearly noted on the electron-microscope photographs obtained with thinned samples (fig. 2). The dispersed particles measure around 200 Å, their form is irregularly rounded, sometimes hexagonal. Ring-shaped reflections on their characteristic diffraction patterns indicate a relatively high degree of recrystallization. Micro-X-ray-spectrographic analysis by means of energy dispersive spectrometer showed that among the predominant mass of particles of pure silver, some contain Cu, Fe, Cr, and Ni, and have ring-shaped reflections not referable to silver. The formation of these ultra-fine polymineralic intergrowths is possible only in a highly viscous medium with a delayed course of the diffusion process. It is not excluded that the finely dispersed silver has a primarily gel nature and that its large dendrites containing relicts of the finely dispersed phase, like the grains with concentric-zoned and fibrous structure, were formed during later processes of recrystallization.

CHEMICAL COMPOSITION OF NATIVE SILVER

The native silver we investigated contains small amounts of admixtures (table 1). The small, irregular forms of the deposits, associated with sulfides of Cu, Fe, and Pb, and with silver-containing sulfosalts, contain admixtures of Sb and Bi, rarely Cu and Fe, whereas the large dendrites of this mineral contain admixtures of Cu, Fe, Cr, and Ni. Determinations of the composition of the admixtures by means of the energy dispersive spectrometer showed that there are no essential differences between their amounts in areas of single-crystal and finely dispersed polycrystalline structure of the deposits of native silver.

The studied samples of native silver contain small amounts of Au (table 1); inclusions of kustelite and electrum noted within their deposits were described in detail by Petrovskaya et al. (1978).

MICRODIFFRACTION AND X-RAY STUDY

Microdiffraction patterns, obtained with thinned platy crystals of silver, for the most part reflected their structural inhomogeneity. Distinctly different were the ring-like reflections from areas of polycrystalline structure (on calculation they correspond to a face-centered cell with $a_0 = 4.08$ Å, characteristic of silver) and the punctuate reflections from single-crystal areas (fig. 2). The character of the punctuate reflections permits one to believe that the single-crystal areas have a two-phase structure. Besides the intense reflections corresponding to the face-centered cubic cell with $a_0 = 4.08$ Å, reflections are present contradicting it. It is known that effects of bombarding crystals with electron beams of high energy are very small and cannot lead to displacement of atoms from their equilibrium position; they lead only to the redistribution of point defects (Hirsch et al., 1968). In this case there is observed on the diffraction pattern a hexagonal net of weaker reflections of the same diffraction pattern that can be referred to the basal plane of a hexagonal phase with parameter $a_0 = b_0 = 2.9$ Å. The evidence that these reflections belong to an independent phase and are not determined by tetrahedral defects of packing in the plane (111), known for face-centered cubic lattices, is based on analysis of the extinctions and intensities of the

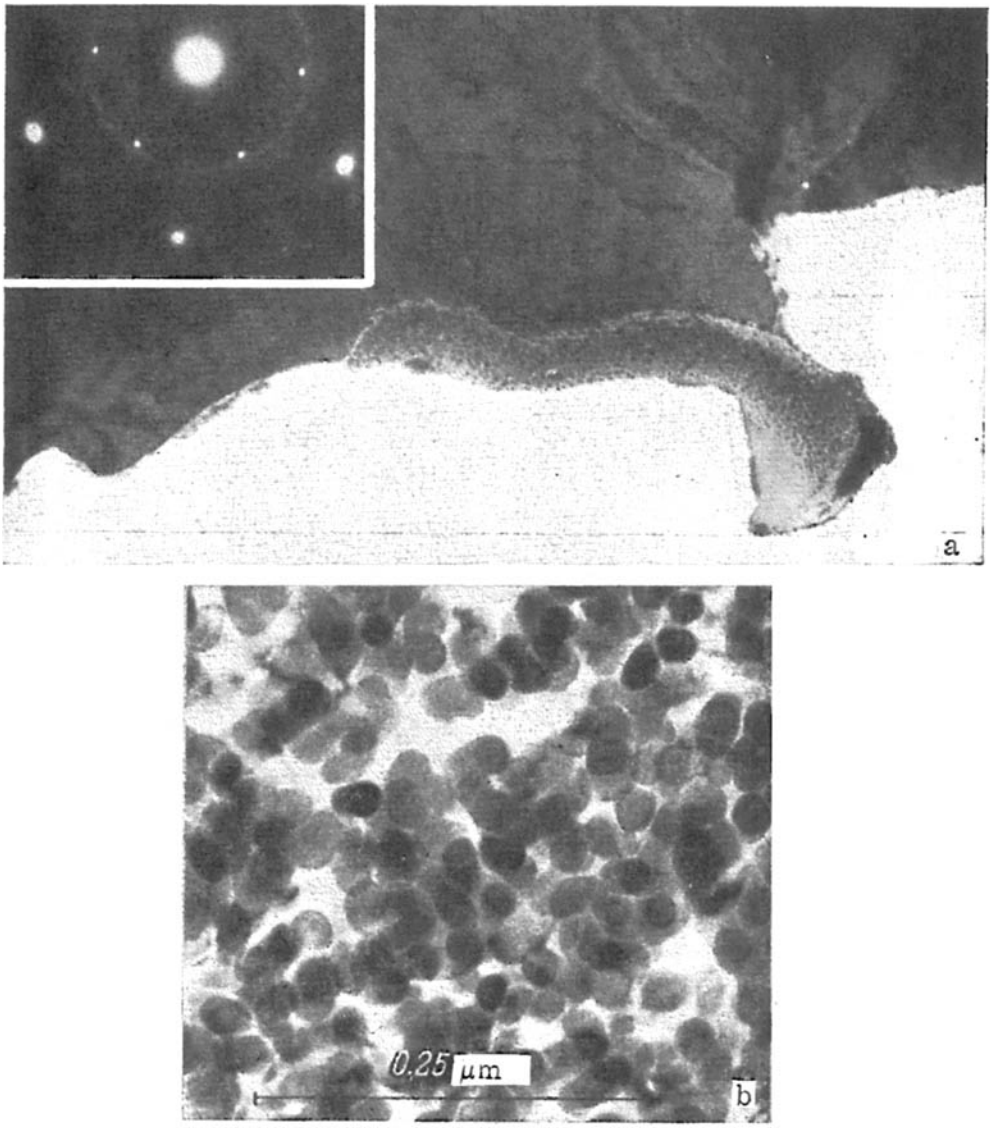

FIGURE 2. Structural inhomogeneity of platy deposits of native silver (a) in areas of polycrystalline structure (b). Electron-microscope photographs with microdiffraction chart of thinned preparations. Magnification: a - x 28,000; b - x 1,000,000.

reflections. The appearance of additional reflections on the diffraction patterns in this case cannot be explained by defects of packing, because thereby changes would be suffered only by those reflections with $(h + k + l) = 3N + 1$, where N is a whole number, whereas reflections of the type (111), the broadening of which can be explained, for example, by the appearance close to the center of the hexagon of additional reflections, are not changed. On most photographs, a net of individual cubic and hexagonal phases of native silver is not obtained, which apparently is explained by their interlayering parallel to the studied plane (111). The relation of the intensities of the reflections of the two phases indicates a significant predominance of the cubic modification.

Attempts at separate visualization of the two structural varieties of silver were made by obtaining their images in reflected light, characteristic for each phase. Figure 3 shows dark images of the same area, obtained respectively in the light of the intense reflection

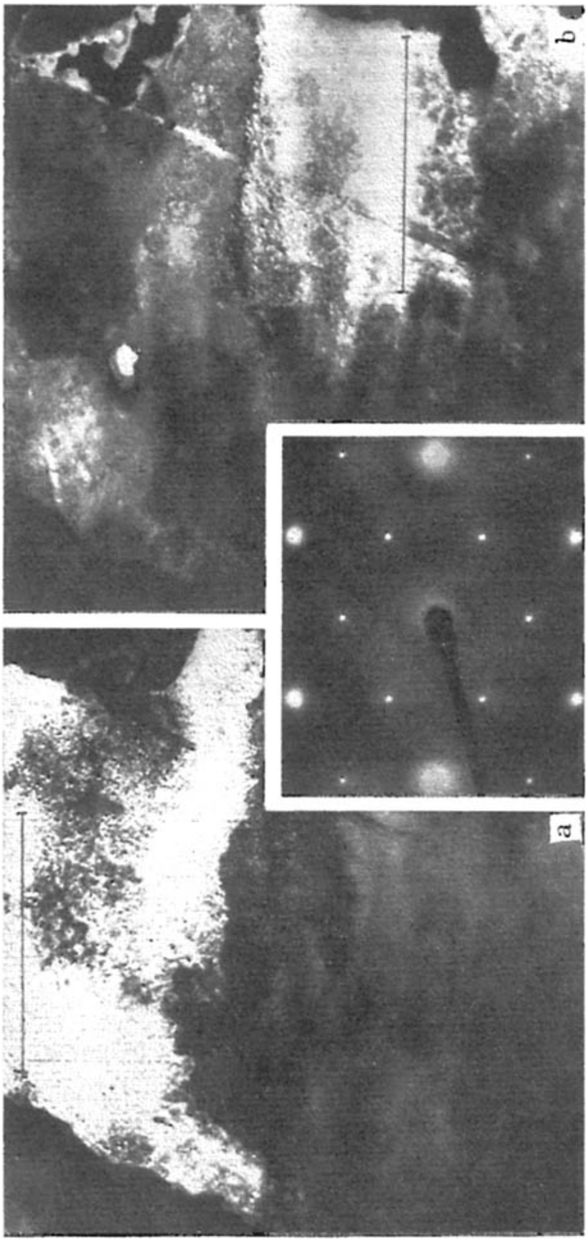

FIGURE 3. Dark images obtained in the light of strong (a) and weak (b) reflections, and microdiffraction pattern of a two-phase area of native silver. Electron-microscope photograph of thinned preparation. Magnification x 40,600.

(220) of the face-centered cubic cell and the weaker reflection $(10\bar{1}0)$ of the hexagonal cell. On the photographs are distinctly differentiated areas referred to the different structural modifications of silver.

In the thinned preparations some fragments consisting mainly of the hexagonal phase of silver were found (fig. 4). This is indicated by the fact that the reflections on the diffraction pattern are more homogeneous in intensity than those of the two-phase area (fig. 3), so that the reflections close to the center of the hexagon of reflections in Figure 4 are even some intense reflections, which may characterize the face-centered cubic lattice. Calculation of the diffraction pattern obtained from plates inclined to the electron beam permitted us to establish the parameter $c_0 \sim 10$ Å, for hexagonal silver. Thus, the hexagonal phase of silver is described by a four-layer structural type ...ABAC... (4H) with parameters a = b = 2.9 Å, $c_0 \sim 10$ Å.

Besides the four-layer hexagonal modification of native silver, predominant among the hexagonal phases, we find occasional monocrystalline areas with a hexagonal phase characterized by the same magnitudes of a_0 and $b_0 = 2.9$ Å, but only half the magnitude of the parameter $c_0 = 4.8$ Å, which does not contradict the assumption of the presence also of a two-layer modification of type ...ABAB... (2H).

The presence of hexagonal phases is confirmed by the X-ray patterns obtained for platy crystals of native silver studied by the microdiffraction method (sample DV-300), and also of its massive deposits (sample DV-260) (table 2). The samples are differentiated by their assembly of minor elements: Cu, Fe, Cr, Ni in DV-300; Sb, Bi, Au in DV-260; the contents of admixtures are indicated in Table 1.

The X-ray patterns of native silver are compared with the interplanar spacings calculated for ideal hexagonal closest packing; the parameters of these ideal structures were calculated, starting from the magnitudes of a_0 for cubic silver, 4.08 Å, and are $a_0 = 2.88$ Å, $c_0 = 9.62$ (for 4-layer packing of type ABAC). In the sample DV-300, in which the hexagonal phase has been satisfactorily established by microdiffraction analysis, the reflections 1.917, 1.634, and 1.008 were not indexed in the cubic symmetry; the second sample gives a still larger number of reflections not characteristic of cubic silver (table 2). These reflections are indexed in the hexagonal symmetry; the measured interplanar spacings are close to the calculated. Lines of the powder patterns belonging to hexagonal phases have weak intensities, which agrees with the data of microdiffraction on the absolute predominance of the cubic modification in the studied samples. The fact that the X-ray pattern of sample DV-260 contains more lines referred to the hexagonal phase indicates, evidently, a larger amount of it in this sample than in sample DV-300.

From the measured interplanar spacings, the parameters of the unit cells of the cubic and hexagonal modifications were calculated (table 2). Silver with admixtures of Cu, Fe, Cr, and Ni is characterized by somewhat larger unit cell parameter ($a_0 = 4.084$ Å), than silver containing Sb and Bi ($a_0 = 4.077$ Å); the parameters of hexagonal cells also differ somewhat (table 2). The latter are notably larger than the theoretical, calculated for ideal hexagonal closest packing. The volume of the cubic unit cell is 67-68 Å^3, of the hexagonal 75.1 Å^3; the X-ray densities are, respectively, 10.5 and 9.5. The specific gravity, measured for platy crystals of native silver (sample DV-300), 10.35, corresponds to a mixture of the two modifications.

The space group $P6_3mc$ is established from the extinction rule; multiples of two for planes of type (0001) and $(hh\overline{2h}l)$, two and three for planes of type $(h\bar{h}0l)$ and $(h0\bar{h}l)$ (table 2).

Table 2 gives the X-ray powder patterns of native silver in comparison with that of the hexagonal ε-phase of the system Ag-Ab — the synthetic analogue of allargentum. Silver containing less than 8-10% Sb retains its cubic structure, in which the unit cell dimensions are larger than those of pure cubic silver (table 2). Dimensions of the hexagonal unit cell of the ε-phase correspond to a two-layer packing model 2H with parameters $a_0 = 2.92$ Å, $c_0 = 4.774$ Å, c/a = 1.632. The interplanar spacings of the structure of the ε-phase, which can also be called hexagonal antimonian silver in two-layer packing, is close to that calculated for pure hexagonal silver in four-layer packing; the indices of the latter differ by doubled magnitudes of l (table 2). Characteristic for the two-layer packing are the reflections 2.38 (0002), agreeing in magnitude of d/n with the reflection (111) of cubic silver, and 1.20 (0004). The latter is present on the X-ray pattern of native silver sample DV-260, which permits one to assume the presence in this sample, besides the four-layer hexagonal modification, also of the two-layer one with parameters $a_0 = 2.93$ Å, $c_0 = 4.79$ Å, c/a = 1.63. The presence of silver 2H in sample DV-300 has been established by microdiffraction.

Thus, our studies permit us to establish new hexagonal modifications for native silver. Because these structural modifications have different sequences of layers in densest packing, they must be referred to polytypes of native silver. In correspondence with the recommendations (Some problems . . . , 1977), it is proposed to designate these structural

TABLE 2. Results of calculation of X-ray patterns of native silver.

Sample DV-300		Sample DV-260		Ag-3C	Ag-4H		Ag-2H (Sb 11%) (ASTM, 2-1145, 1952)		ε-phase	Supergene Ag (Chebotarev et al., 1976)		Antimonian silver (6% Sb) (Somachi and Clark, 1966)
I	*d/n*	*I*	*d/n*	*hkl*	*hkil*	*d/n*	*I*	*d/n*	*hkil*	*I*	*d/n*	*d/n*
—	—	5	2.721	—	—	—	—	—	—	4	2.88	—
4	2.602	6	2.588	111β	$10\bar{1}0$ 0004	2.50	100	2.53	$10\bar{1}0$	4	2.56	—
—	—	1	2.443	—	$10\bar{1}1$	2.425	—	—	—	—	—	—
10	2.360	10	2.349	111	—	—	60	2.38	0002	10	2.35	2.37
—	—	1	2.241	—	$10\bar{1}2$ $1\bar{1}02$	2.236	100	2.24	$10\bar{1}1$	2	2.26	—
2	2.039	8	2.036	002	$10\bar{1}3$	2.00	—	—	—	9	2.04	2.059
2	1.917	1	1.875	—	$10\bar{1}4$ 1104	1.767	40	1.74	$10\bar{1}2$	—	—	—
1	1.634	1	1.668	—	0006	1.666	—	—	—	2	1.659	—
1	1.591	6	1.587	220β	—	—	—	—	—	1	1.596	—
—	—	1	1.526	—	$10\bar{1}5$	1.561	—	—	—	—	—	—
10	1.444	10	1.443	220	$11\bar{2}0$	1.443	80	1.46	$11\bar{2}0$	9	1.450	1.455
1	1.360	2	1.358	311β	$11\bar{2}2$ $10\bar{1}6$	1.386	80	1.35	$10\bar{1}3$	2	1.366	—
1	1.303	2	1.300	222β	—	—	—	—	—	—	—	—
—	—	2	1.286	—	$11\bar{2}4$	1.270	60	1.25	$11\bar{2}2$	—	—	—
10	1.231	10	1.229	311	$20\bar{2}1$	1.240	60	1.23	$20\bar{2}1$	9	1.238	1.241
—	—	1	1.213	—	$20\bar{2}2$	1.212	—	—	—	—	—	—
—	—	1	1.199	—	—	—	20	1.20	0004	—	—	—
9	1.181	9	1.178	222	$20\bar{2}3$	1.170	—	—	—	6	1.184	1.188
1	1.128	1	1.160	—	$20\bar{2}4$	1.118	20	1.12	$20\bar{2}2$	—	—	—
2	1.033	4	1.033	133β	—	—	20	1.08	$10\bar{1}4$	4	1.036	—
2	1.0285	4	1.021	400	—	—	—	—	—	3	1.023	—
2	1.008	2	0.990	—	$20\bar{2}6$	1.00	40	0.99	$02\bar{2}3$	3	1.010	—
—	—	—	—	133	—	—	40	0.94	$21\bar{3}1$	—	—	0.946
—	—	—	—	—	—	—	40	0.93	$11\bar{2}4$	—	—	—

Unit cell parameters

				Ag-3C				
a_0	4.084	4.077	—	—	—		4.092	4.115
$V (Å)^3$	68.12	67.76	—	—	—		—	—
$\rho_{(X\text{-ray})}$	10.51	10.57	—	—	—		—	—
				Ag-4H				
a_0	2.94	2.93	—	2.88	—		—	—
c_0	10.11	10.18	—	9.62	—		—	—
$1/2c/a$	1.72	1.73	—	1.63	—		—	—
$V(Å)^3$	75.15	75.15	—	—	—		—	—
$\rho_{(X\text{-ray})}$	9.53	9.53	—	—	—		—	—
				Ag-2H				
a_0	2.94	2.93	—	—	2.92		—	—
c_0	4.80	4.79	—	—	4.774		—	—
c/a	1.63	1.63	—	—	1.632		—	—
$V (Å)^3$	—	35.40	—	—	—		—	—
$\rho_{(X\text{-ray})}$	—	10.11	—	—	—		—	—

Note. Conditions of photograph: RKU camera (3R = 114 mm), diameter of rubber sphere 0.2 mm, unfiltered Fe radiation.

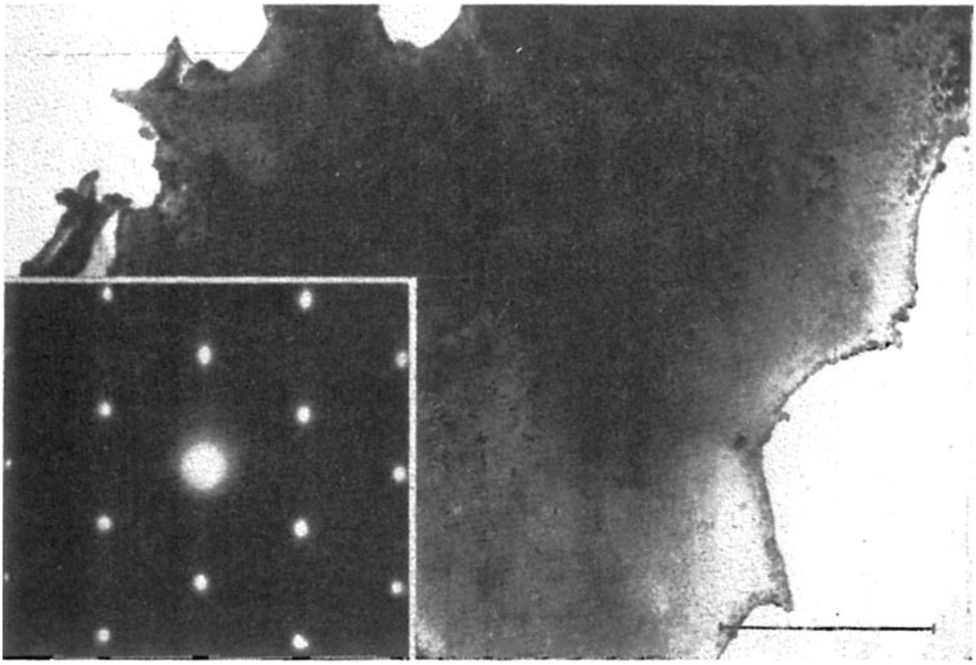

FIGURE 4. Electron microscope image of the hexagonal phase of silver (Ag-4H) and the microdiffraction pattern of the plane (10-10) [sic]. Magnification x 32,000.

modifications as silver-2H (two-layer hexagonal packing) and silver-4H (four-layer hexagonal packing), in distinction from cubic silver with face-centered cell (silver 3C). Regular intergrowths of different polytypes in the same crystals of silver were formed according to the rule of parallel planes (111) of the cubic modification and the basal plane ($10\bar{1}0$) of the hexagonal modification. It is evident that the formation of different polytypic modifications occurred under the same physicochemical conditions of mineral formation; their origin, most probably, is connected with growth phenomena. The polytypy of native silver was aided by slow crystallization from a primary gel material; it is not excluded that the hexagonal modifications are metastable formations of an early stage of growth. This may be especially indicated by the sharp decrease of the frequency of occurrence of the silver polytypes in the order 3C-4H-2H. Errors in the sequence of the superposition of layers originating during the growth of silver-4H (...ABAC...) and silver-2H (...ABAB...) were probably stabilized by admixtures, mainly Sb, Bi, Cu, and Fe. At the same time, one cannot state that the admixtures are the principal factor in the origin of the non-cubic polytypes of silver; varieties are known containing the same admixtures in far greater amounts and keeping the cubic structure (Minerals, 1960).

The distribution of the hexagonal modifications of silver is apparently not restricted to ores of the deposits discussed. Thus, Chebotarev et al. (1976) give an X-ray powder pattern of supergene silver from a gold deposit of Uzbekistan, in which some of the interplanar spacings (2.26, 1.659, 1.010, table 2) refer to a possible hexagonal phase mixed with the cubic.

PHYSICAL PROPERTIES

We studied the dispersion of the reflectance and the variation of hardness by microimpression for the native silver. The reflectivity was measured by L. N. Vyal'sov on the "PIOR" apparatus (Leitz 3b objective with effective aperture 0.1, direction of vibration of polarizer perpendicular to the plane of incidence). Standard—pyrite. The relative error of measurement is ±2%. The grains of native silver are isotropic; birefringence and anisotropy not observed in air, which is explained by the absolute predominance of the cubic modification in the samples. The reflectance is notably lower than that given in handbooks (Bezsmertnaya et al., 1973); the character of the dispersion of reflectance (R, %) in the visible region of the spectrum (wave length, nm) is analogous to that known for native silver (fig. 5): 67.0 — 440;

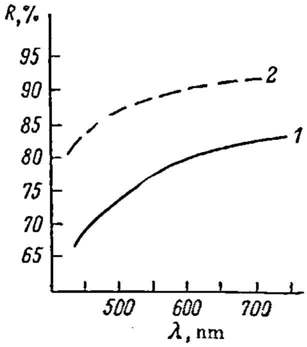

FIGURE 5. Curves of dispersion of reflectance of native silver. 1 - platy deposit of mixture of cubic and hexagonal modifications; 2 - after Bezsmertnaya et al. (1966).

69.4 — 460; 71.5 — 480; 73.6 — 500; 75.0 — 520; 76.5 — 540; 77.8 — 560; 78.8 — 580; 79.6 — 600; 80.2 — 260; 80.9 — 640; 81.5 — 660; 82.0 — 680; 82.5 — 700; 83.0 — 720; 83.5 — 740.

The hardness of native silver was measured on a PMT-3 microsclerometer, standardized with NaCl. According to 50 measurements on 10 samples, the magnitudes of hardness vary within the range 51-59, average 53.5 ± 5 kg/mm^2. The form of indentations is isotropic.

CONCLUSIONS

1. In gold-silver ores of a deposit in Northeast USSR new hexagonal modifications were found in native silver, occurring in regular intergrowth with cubic silver. The new modifications are polytypes Ag-2H (a = 2.93 ± 0.01 Å, c_0 = 4.79 ± 0.01 Å, c/a = 1.63, d. X-ray = 10.11) and Ag-4H (a_0 = 2.93 ± 0.01 Å, c_0 = 10.11 ± 0.04 Å, 1/2 c/a = 1.72, d. X-ray = 9.53). The unit cell parameter of cubic silver (Ag-3C) with admixtures of Cu, Fe, Cr, and Ni is 4.084 ± 0.005 Å, that with admixture of Sb, Bi, Au is 4.077 ± 0.005 Å. The measured specific gravity of a mixture of cubic and hexagonal modifications of native silver is 10.35. The amount of the polytypes of silver in their natural mixtures decreases sharply in the order 3C-4H-2H. The rule of intergrowth is 111 (3C) $10\bar{1}0$ (4H, 2H).

Characteristic for the hexagonal silver are the following X-ray lines: 2.241, 1.668, 1.286, 1.213, 1.199, 1.160, 1.00.

2. The natural polytypes of native silver are possibly the cause of the low solubility in silver of the structurally similar analogues of its cubic modification—gold and copper.

3. The polytypes of silver were formed during the recrystallization of finely dispersed deposits of this mineral, having a primary gel nature. It is possible that these hexagonal polytypes are metastable formations, the origin of which is determined by the slow speed of growth of the crystalline individuals. Admixtures, present in the silver in amounts of tenths of a percent, play the role of stabilizers of errors in the sequence of superposition of the layers of the crystal structure.

4. Silver-containing mineral associations were formed in the late stages of the process of ore deposition in gold-silver ores at small depth. We can distinguish a narrow paragenesis of native silver with late generation of pyrite, chalcopyrite, galena, tetrahedrite-tennantite, and an orthogenetic association of this mineral with argentite and complex silver sulfosalts.

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