

Hexaferrum – (Fe, Ru), (Fe, Os), (Fe, Ir) – new mineral.

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A hitherto unreported mineral was discovered in chromitites of the Chirynaisky dunite-harzburgite complex in the Koryak Highland (Far East Russia) – it represents a solid solution of Fe and Ru, Fe and Os, and Fe and Ir (Mochalov et al. 1985). Also, this mineral had been found in many of the related complexes of dunite-peridotite, in the ophiolite belts worldwide (Stockman & Hlava 1984, Dmitrenko et al. 1985, Palandzhyan et al. 1994; etc.). These solid-solutions of the PGE with Fe are substantially rich in Ru (Fe, Ru), Os (Fe, Os), or Ir (Fe, Ir), with Fe > Ru, Fe > Os, and Fe > Ir (expressed in at.%); they all have a hexagonal close packed structure, space group $P6_3/mmc$, with the cell parameters (in Å): a = 2.64, c = 4.20; a = 2.59, c = 4.16, and a = 2.61, c = 4.22, respectively. In accordance with the nomenclature, approved for native alloys by the CNM IMA (Harris & Cabri 1991), these solid-solutions of various PGE with Fe correspond to one and the same species: native iron with the hexagonal symmetry. Thus, the mineral name, hexaferrum, was given on the basis of the observed chemical composition and structural type of the new mineral. The following varieties exist for this species of hexaferrum: ruthenian (Ru > Os, Ir; at.%), osmian (Os > Ru, Ir) and iridian (Ir > Ru, Os).

Mode of occurrences. The Chirynaisky complex (Koryak Highland; Fig. 1), in which the new mineral was discovered and characterized for the first time in detail, has a blocky structure. It is composed of harzburgite, with subordinate dunite, which host schlieren- and vein-type bodies of pyroxenites (orthopyroxenite, i.e., enstatite, websterite and clinopyroxenite). Dunite is developed as numerous pods (“lenses”), oriented conform (or “concordantly”) with respect to the igneous foliation (or “banding”) existing in the harzburgite. Dunite and harzburgite are slightly serpentinized, and display a blastic micro-texture; their rock-forming minerals are highly magnesian and having low values of the *f* index: 6 – 9 mol.%. [I guess they mean: $f = 100(\text{FeO} + \text{Fe}_2\text{O}_3)/(\text{FeO} + \text{Fe}_2\text{O}_3 + \text{MgO})$]. Chromite segregations vary from disseminated to schlieren- or vein-shaped; they are related with dunite and harzburgite. The chromite grains are rich in the magnesiochromite component (up to 67 mol.%) and display a tendency of increase in the spinel component in compositions of chromite associated with the harzburgite. Accessory grains of PGM are located in the chromitites.

The PGM occur as inclusions in grains of chromian spinels to form mutual intergrowths of hypidiomorphic texture. The PGM grains-sizes do not exceed 200 μm ; the grains ranging 5 to 50 μm dominate. The distribution of the PGM grains is extremely inhomogeneous, from single grains to several hundreds. The bulk of them (55%) are represented by fibrous aggregates of hexaferrum-(Ru). Commonly, aggregates of hexaferrum-(Ru) have a cubic (Fig. 2) or octahedral habit (Fig. 3). Such patterns represent negative inclusions occurring in chromian spinels (Fig. 3) or are pseudomorphs after laurite (Fig. 2).

Hexaferrum-(Os) typically forms monomineralic grains. Hexaferrum-(Ir) is rarest; commonly, it is associated with hexaferrum-(Ru) and hexaferrum-(Os), and also with an iridian taenite (Fe, Ir) having a cubic structure (Fig. 4). Hexaferrum is accompanied by other PGM – iridosmine, rutheniridosmine, osmiridium, laurite, and, occasionally, tulameenite, and solid solutions of the composition (Fe, Rh, Ir) and (Ni, Fe, Ir). In some cases, the PGM grains are accompanied, in the chromitite schlieren, by the other native alloys: awaruite (most common), native iron, copper, zinc, compounds of Cu and Zn, Pb and Sn, as well as by sulfides and arsenides: pentlandite, pyrrhotite, heazlewoodite, millerite, and oregonite. Admixtures of the PGE (mostly Pt and Ir, less commonly Rh, Pd, and Ru) are not so rare in compositions of awaruite and Fe-Ni sulfides.

Physical properties. Under the binocular microscope, the hexaferrum grains look like isometric crystals, which exhibit faces (3-, 4-, 5-, and of hexahedral shapes). Their color is steel gray, from light to dark, with yellowish tints and metallic luster. The grains are slightly magnetic to magnetic. The mineral is brittle, and, under pressing, is crushed to form a black powder. The cleavage is not observed. The mineral is not affected by standard chemicals and nitrohydrochloric acid.

There is a difference, observed in reflected light, between the compositional varieties of hexaferrum: (Fe, Ru), (Fe, Os), and (Fe, Ir).

Grains of hexaferrum (Ru) are light-gray and are notably darker than those of hexagonal and cubic solid-solutions of Os, Ru and Ir. In the scale of polished section, individual grains could be distinguished, having different colors (white, light-gray and gray). Single grains, with different levels of reflectance, are fairly common (Fig. 5a). This effect is owing to the inhomogeneous distribution of porosity in the grains (5b, c). The darker grains, or their portions,

show a higher extent of porosity. Micro-fractures (or micro-pores) are slightly curved; they cross each other under angles of 60° and 120°.

The bireflectance is absent. The mineral is strongly anisotropic, with color effects from light blue-gray to brown-yellow. The grains and “crystals” of hexaferrum-(Ru) display a mosaic extinction, which is resulted from their micro-aggregate textures, with the development of fine intergrowths of individual platy-like grains (Fig. 2b). The reflectance value of hexaferrum-(Ru) is notably lower than that of metallic ruthenium (Table 1); their patterns of dispersion of reflection also differ (Table. 1, Fig. 6, 1, and 3).

Under reflected light, hexaferrum-(Ru) is white, slightly anisotropic, without color (pleochroic) effects. The reflectance spectrum is somewhat concave in shape, showing a minimal value at 520 – 600 nm. This curve differs essentially from that of native osmium: two maximums are observed, one in the shortwave range, like that of native osmium, and also in the long wave area of the spectrum, as for iron (Table. 2, Figs. 6, 2, 4, 5).

Hexaferrum-(Ir) is white to light-gray in color. The darkest (grayest) grains (and their portions) have a notably fractured surface. It is slightly anisotropic; pleochroism or bireflectance are not observed. The abundance of micro-fractures and inclusions of iridian taenite precluded us from making measurements of its reflectance and microhardness values.

The measured values of microhardness for hexaferrum-(Ru) are 629 – 679, with a mean of 652 kg/mm² (“PMT-3” tester; P = 50; n = 6 for 2 grains). Thus, it is, in fact, close to metallic ruthenium, which gave a range 529 – 768, mean 655 kg/mm² (P = 100, n = 18). Hexaferrum-(Os) is harder; its range is 741 – 880, and the mean value is 810 kg/mm² (P = 50, n = 9, for 3 grains).

Hexaferrum-(Os) has a lower hardness, if compared with native osmium: 1097 kg/mm² (P = 100; n=10). Judging from the relative relief, hexaferrum-(Ir) is close in its hardness to hexaferrum-(Ru); however, it is less hard than hexaferrum-(Os).

Chemical composition of the new mineral varies considerably:

- 1) in fact, a complete (continuous) range of compositions was documented for the naturally occurring phases varying from hexaferrum-(Ru) to Fe-rich ruthenium, and also from hexaferrum-(Ru) to hexaferrum-(Os);
- 2) The Ir content in these alloy minerals does not exceed 15 wt.% (6 at.);

- 3) Levels of admixtures of Os and Ru in hexaferrum-(Ir), as a rule, are less than 1 wt.% (0.5 at.%);
- 4) The Fe content in hexaferrum-(Ir) ranges from 55 to 77 at.%, which is compatible with the stability areas observed for the ξ - and γ -phases in the system Fe-Ir (Re: "Noble metals 1984") (Fig. 7; a, b, Table 3).

The following admixture elements are not uncommon in hexaferrum: Pt, Rh, Pd, Ni, Co, and Cu (Table. 3). Besides, varying amounts (1-2%) of Mg, Si, S, and As are not uncommon. Typically, the elements of latter group are heterogeneously distributed, being characteristic for the most porous grains of hexaferrum. Thus, these likely reflect the presence of sub-micrometric inclusions composed of silicates, sulfides, and arsenides, which fill the spaces within micropores and micro-fractures in grains of the mineral.

Electron-microprobe analyses of many grains of hexaferrum display a deficit in their totals; this feature is most characteristic of hexaferrum-(Ru). It should be noted that light elements (C, O, N, and F) were not analyzed in this study (Camebax microprobe, the limit of detection 3 wt.%). The observed deficit in analytical totals is likely a reflection of the porosity of these grains.

X-ray data. The X-ray powder patterns were obtained for monomineralic grains of hexaferrum-(Ru) and hexaferrum-(Os), which were crushed. These patterns are identical to those of metallic ruthenium and osmium, having the hexagonal close-packed structure (Tables 4, 5). The cell parameters of hexaferrum-(Ru) and hexaferrum-(Os) are less than those of these metals. This characteristic is explained by the isomorphous incorporation of Fe in structure of the new mineral; indeed, the atomic radius of Fe is less than those of Ru and Os ("Noble metals, 1984").

The Debye–Scherrer diffraction patterns, obtained for monomineralic grains-(micro-aggregates) of hexaferrum-(Ir), gave broader reflections (Table. 6). The calculated values of cell parameters of hexaferrum-(Ir) are compared well with those of the ξ -phase known in the Fe – Ir system ("Noble metals, 1984"). By analogy with synthetic ξ -phase, hexaferrum has the hexagonal close-packed structure, space group $A3(Mg)$, $P6_3/mmc$, and $Z = 2$.

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Specimens of hexaferrum-(Ru) and hexaferrum-(Os) were provided to the Mining Museum (Saint Petersburg, Russia).

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¹ Original article shows "Ibid.", wrongly assigning this to Can. Mineral.

Fig. 1. Schematic geological map of the Chirynaisky massif (after Dmitrenko et al. 1985).

- 1) Eocene Epoch: aleurolite, sandstone, gravelite (or gritstone), and conglomerate.
- 2) Late Jurassic - Early Carboniferous (?): basalt, andesite, tuff, tuff breccias, argillite, aleurolite, jasper.
- 3, 4) a complex of metamorphosed peridotite (magnesian dunite-harzburgite association). 3: Dunite, 4: Harzburgite, with their strike and dip of foliation.
- 5, 6) Taxite complex (ferrous dunite-peridotite-pyroxenite association). 5) Schlieren and banded interlayering of websterite, clinopyroxenite ("diopsidite"), lherzolite, and dunite, with their strike and dip of foliation (banding). 6) The same, including gabbro.
- 7) Gabbronorite, magnesian gabbro.
- 8) Tonalite, plagio-granite.
- 9) Serpentinite mélange.
- 10) Intrusions and dykes of diabase.
- 11) Boundaries of facial zones.
- 12) Faults.
- 13) Platinum-bearing chromitite (with numbers of specimens). "KIII" is Mount Krasnaya Shapochka.

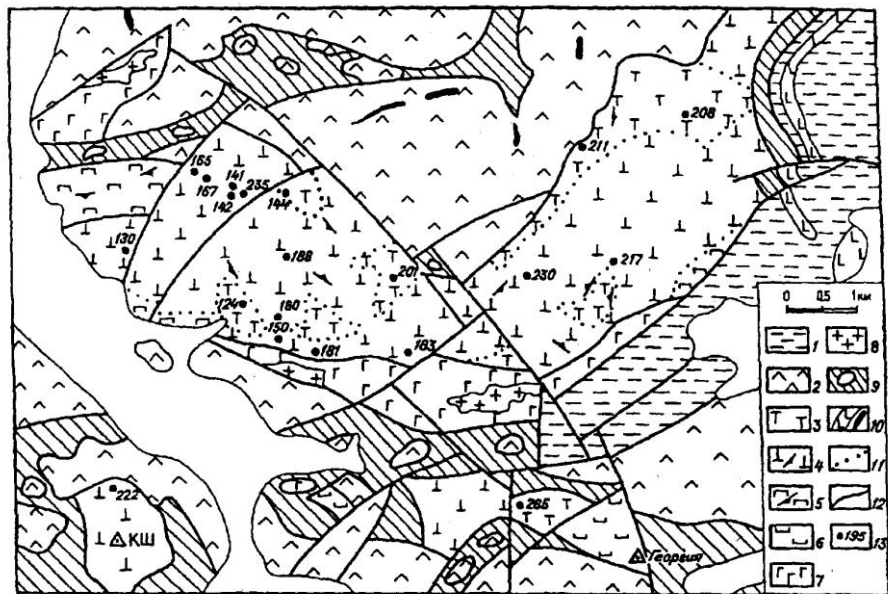


Fig. 2. The aggregate of hexaferrum "crystals": a) a secondary-electron image, Camebax microprobe, magn. 1200; b) a reflected-light photograph. 1: hexaferrum-(Ru), 2: hexaferrum-(Os), 3: Iridium (Fe-bearing); polished section; crossed nicols; magn. 420.

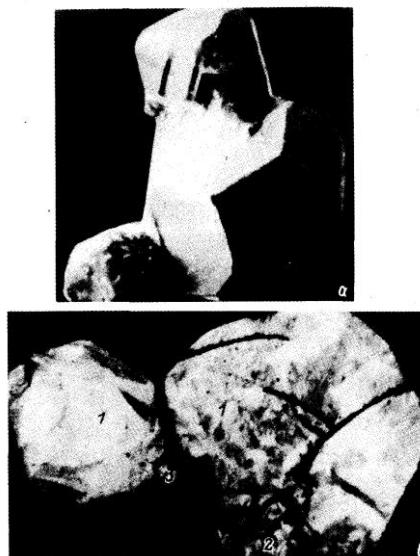


Fig. 3. A “negative crystal” of hexaferrum-(Ru) of octahedral shape, which is enclosed within a chromian spinel. a) hexaferrum “crystal” with imprints left (maid) of faces of the associated chrome spinel; b) a polished section showing the association of iridosmine (Os, Ir), chromian spinel (Sp), and serpentine (Spt). The scale bar is 10 micrometers.

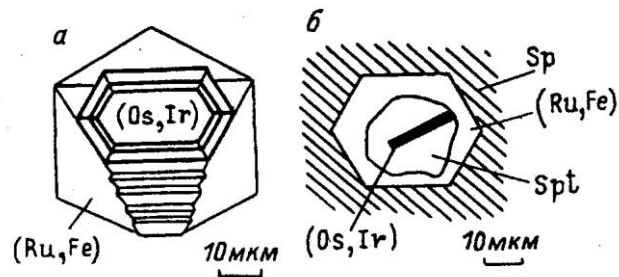


Fig. 4. The aggregate of grains of hexaferrum (of different compositional varieties) and iridian taenite. 1: hexaferrum-(Os), 2: hexaferrum-(Ir), 3: iridian taenite. Secondary-electron image, magn. 50 (Camebax microprobe).

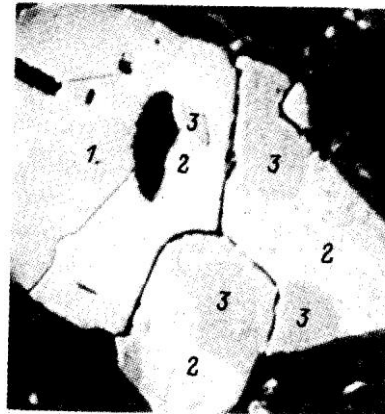


Fig. 5. Patterns of porosity of hexaferrum grains; a, b: heterogeneous grains of hexaferrum-(Ru) having different reflection (darker grains are more porous). Polished section, magn. 400; a) specimen 48-18, b) 48-108; c) Absorbed-electron image; magn. 1500 (Camebax).

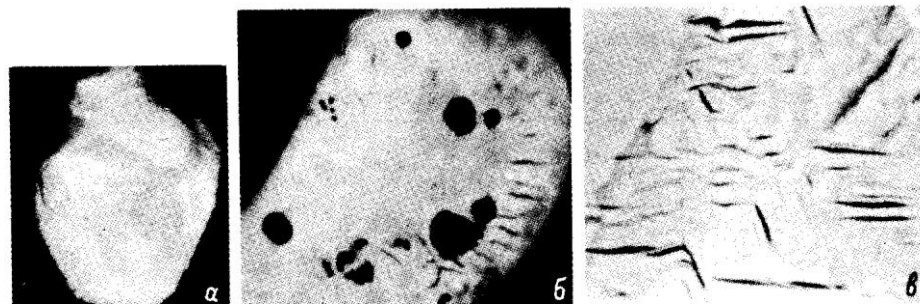


Fig. 6. Reflectance spectra for hexaferrum-(Ru) (1) and hexaferrum-(Os) (2), in comparison with metallic ruthenium (3), native osmium (4) and iron (5), on the basis of data listed in Tables 1 and 2.

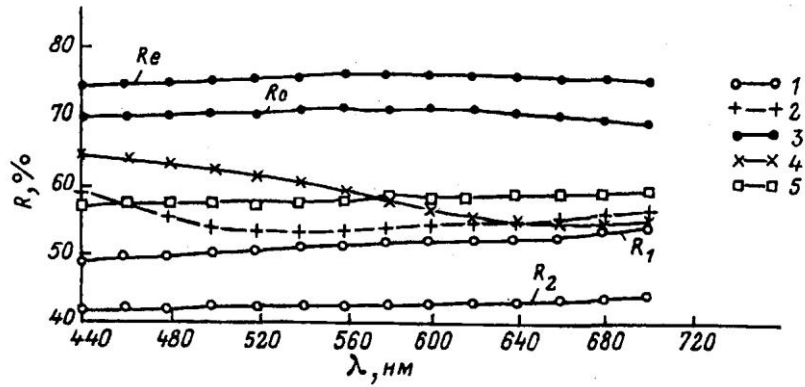


Fig. 7. Diagram showing relationships of mineral-forming elements in hexaferrum. a) ruthenium, osmium and totals of iron, copper and nickel; the dotted line designates the established fields of compositions (Fe, Ru), (Fe, Os), (Ru, Fe) and (Fe, Ru, Os), and the miscibility gap in the phase diagrams Ru-Fe and Os-Fe between phases of hexagonal and cubic symmetry (“Noble Metals”, 1984); b) osmium, ruthenium and iridium; 1) Chirynaisky massif, 2) Krasnogorsky massif, 3) Srednegorsky massif, 4) Elistratovsky massif.

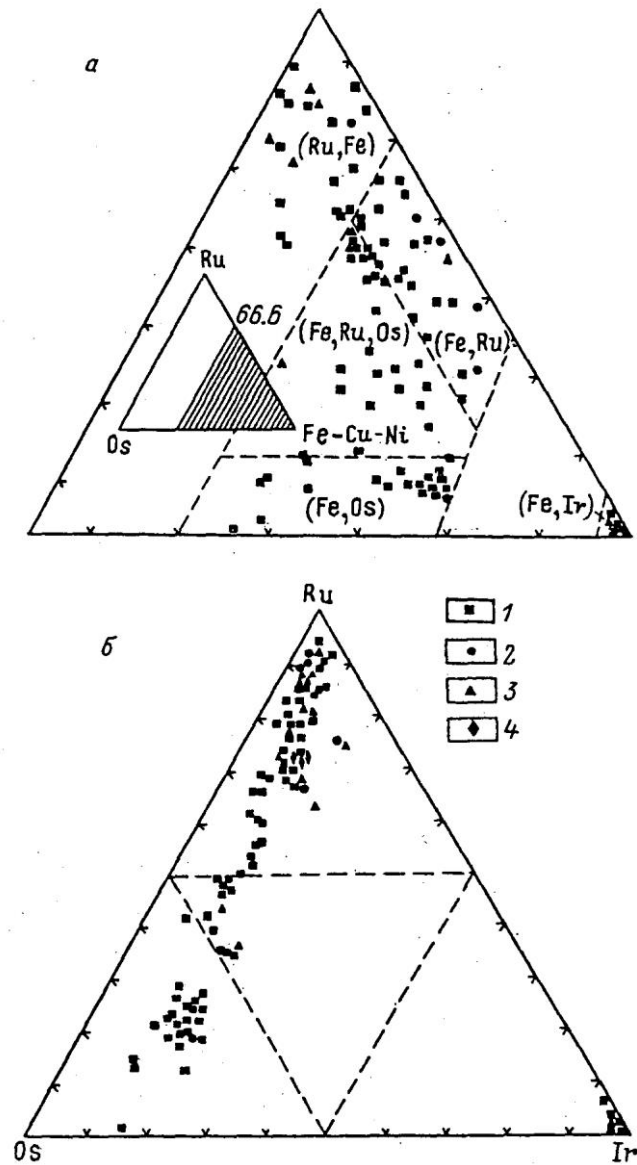


Table 1. Reflectance values for hexaferrum-(Ru) and synthetic ruthenium;

Reflection (R, %) of hexaferrum-(Ru) and synthetic ruthenium				
λ , нм	Гексаферрум-(Ru), обр. 48-245		Рутений	
	R_1	R_2	R_0	Re'
440	49.6	41.8	70.2	73.9
460	49.6	41.8	69.6	73.4
480	49.8	41.9	69.6	74.0
500	50.1	42.0	69.6	74.2
520	50.4	42.0	70.0	75.0
540	50.6	42.0	70.7	75.4
560	51.1	42.0	71.2	76.1
580	51.4	42.0	71.3	76.1
600	51.9	42.0	71.5	76.0
620	52.3	42.2	70.8	75.6
640	52.8	42.4	70.5	75.6
660	53.4	43.0	70.1	75.5
680	53.9	43.4	69.6	75.4
700	54.6	44.0	69.3	75.1

Table 2. Reflectance values for hexaferrum-(Os), native osmium and native iron;

Reflection (R, %) of hexaferrum-(Os), native osmium and native iron			
λ , нм	Гексаферрум-(Os)	Самородный осмий	Самородное железо
440	58.5	64.1	56.6
460	57.0	63.7	57.0
480	55.1	63.1	57.2
500	54.3	62.2	57.2
520	54.3	61.1	57.1
540	53.4	60.1	57.0
560	53.4	58.9	57.0
580	53.2	57.5	57.0
600	53.5	56.6	57.0
620	53.6	55.5	57.4
640	54.2	55.0	57.9
660	54.7	54.4	58.2
680	55.2	54.0	58.8
700	56.0	53.8	59.3

Table 3. Chemical composition of hexaferrum (wt.%). Notes: MS-46 Cameca microprobe (no. 1-6); Camebax (no. 7-11). Accelerating voltage is 20 kV, beam current is 30 nA, beam size: 2-4 micrometers. Standards: pure metals. X-ray lines: $L\alpha$ for the PGE, and $K\alpha$ for all of the other elements. Empirical corrections (on the basis of standards) were made for Cu, Rh and Os, because of their peak overlaps with the lines of Ir, Ru, and Cu.

Chemical composition of hexaferrum (wt %)													
№ ан.	№ обр.	Формула	Pt	Ir	Os	Ru	Rh	Pd	Fe	Ni	Cu	Co	Сумма
1	48-90	(Fe _{0.68} Ru _{0.20} Os _{0.09} Ir _{0.02} Ni _{0.01})	He обн.	4.44	20.6	25.0	He обн.	He обн.	48.1	0.88	He обн.	0.05	99.07
2	48-43	(Fe _{0.69} Ru _{0.17} Os _{0.09} Ir _{0.04})	0.12	8.46	22.2	21.5	* *	* *	47.8	0.03	* *	0.14	100.25
3	48-126	(Fe _{0.49} Ru _{0.34} Os _{0.10} Ir _{0.05})	0.28	9.01	20.9	36.9	* *	* *	29.4	0.09	0.22	0.15	96.95
4	117-8	(Fe _{0.69} Os _{0.18} Ru _{0.06} Ir _{0.05} Ni _{0.02})	0.19	9.89	38.0	6.55	* *	* *	43.8	1.49	He обн.	He обн.	99.92
5	117-12	(Fe _{0.71} Os _{0.17} Ru _{0.06} Ir _{0.05})	0.11	9.91	37.1	6.92	0.32	* *	45.2	0.17	* *	0.06	99.79
6	117-20	(Fe _{0.68} Os _{0.20} Ru _{0.06} Ir _{0.05})	0.30	10.0	40.4	6.73	He обн.	* *	40.7	0.10	* *	0.05	98.28
7	48-11	(Fe _{0.63} Ir _{0.28} Rh _{0.05} Ru _{0.02})	1.02	48.8	0.11	1.82	4.42	* *	31.6	0.50	* *	0.02	88.29
8	76-3	(Fe _{0.58} Ir _{0.34} Cu _{0.06} Ni _{0.01} Pt _{0.01})	2.12	60.7	He обн.	He обн.	0.82	* *	29.7	0.71	2.81	0.03	96.89
9	117-13	(Fe _{0.69} Ir _{0.26} Pt _{0.03} Cu _{0.01})	5.01	51.6	0.54	* *	0.72	* *	39.8	0.43	0.91	0.02	99.03
10	119-21	(Fe _{0.69} Ir _{0.29})	0.62	57.3	He обн.	0.13	0.44	* *	40.2	0.50	0.40	0.10	99.69
11	119-23	(Fe _{0.74} Ir _{0.23} Ni _{0.02})	1.04	49.6	0.51	He обн.	0.62	0.13	46.1	1.20	He обн.	He обн.	99.20

Table 4. X-ray powder (Debye-Scherrer) patterns for hexaferrum-(Ru) and synthetic ruthenium (Note: 57.3-mm camera; FeK radiation).

Гексаферрум-(Ru), обр. 48-126			Рутений (ASTM, № 6-0663)		<i>hkl</i>
<i>I</i>	$d_{\text{сизм}}$	$d_{\text{орвсч}}$	<i>I</i>	$d_{\text{сизм}}$	
5	2.28	2.29	41	2.343	10 $\bar{1}$ 0
6	2.10	2.10	37	2.142	0002
10	2.006	2.008	100	2.056	10 $\bar{1}$ 1
3	1.549	1.547	23	1.5808	10 $\bar{1}$ 2
3	1.316	1.320	25	1.3530	11 $\bar{2}$ 0
3	1.195	1.194	24	1.2189	10 $\bar{1}$ 3
			5	1.7150	20 $\bar{2}$ 0
2	1.118	1.118	26	1.1434	11 $\bar{2}$ 2
2	1.108	1.103	20	1.1299	20 $\bar{2}$ 1
			4	1.075	0004
			7	1.0278	20 $\bar{2}$ 2

Параметры элементарной ячейки (Å)

$$a = 2.64 \pm 0.01 \quad a = 2.7058$$

$$c = 4.20 \pm 0.02 \quad c = 4.2819$$

Рентгеновская плотность (г/см³)

$$10.69 \quad 12.43$$

Table 5. X-ray powder (Debye-Scherrer) patterns for hexaferrum-(Os) and synthetic osmium.

Гексаферрум-(Os), обр. 117-8			Осмий (XRDC, 1976, № 6-0662)		<i>hkl</i>
<i>I</i>	$d_{\text{сизм}}$	$d_{\text{орвсч}}$	<i>I</i>	$d_{\text{сизм}}$	
5	2.246	2.244	3	2.367	10 $\bar{1}$ 0
6	2.087	2.084	3	2.160	0002
10	1.976	1.976	10	2.076	10 $\bar{1}$ 1
4	1.528	1.527	2	1.535	10 $\bar{1}$ 2
6 ш	1.297	1.295	2	1.3668	11 $\bar{2}$ 0
6 ш	1.180	1.181	2	1.2300	10 $\bar{1}$ 3
			1	1.1840	20 $\bar{2}$ 0
5 ш	1.100	1.100	2	1.1510	11 $\bar{2}$ 2
3 ш	1.083	1.083	2	1.1416	20 $\bar{2}$ 1
1	1.042	1.042	1	1.0799	0004
			1	1.0383	20 $\bar{2}$ 2

Параметры элементарной ячейки (Å)

$$a = 2.591 \pm 0.001 \quad a = 2.7341$$

$$c = 4.168 \pm 0.002 \quad c = 4.3197$$

Объем элементарной ячейки (Å³)

$$24.22 \pm 0.3 \quad 27.96$$

Рентгеновская плотность (г/см³)

$$12.09 \pm 0.02 \quad 22.75$$

Table 6. X-ray powder (Debye-Scherrer) pattern for hexaferrum-(Ir). (Note: 57.3-mm camera; CuK radiation).

Calculated data for debayegrams of hexaferrum-(Ir)						<i>hkl</i>
Обр. 48-11			Обр. 76.3.1			
<i>I</i>	$d_{\text{снзм}}$	$d_{\text{орасч}}$	<i>I</i>	$d_{\text{снзм}}$	$d_{\text{орасч}}$	
5 ш	2.254	2.257	5 ш	2.266	2.266	10 $\bar{1}$ 0
7 ш	2.103	2.108	7 ш	2.113	2.113	0002
10 ш	1.993	1.989	10 ш	1.998	1.997	10 $\bar{1}$ 1
4 ш	1.542	1.540	4 ш	1.544	1.546	10 $\bar{1}$ 2
5 ш	1.304	1.303	5 ш	1.308	1.309	11 $\bar{2}$ 0
4 ш	1.192	1.193	4 ш	1.196	1.196	10 $\bar{1}$ 3
4 ш	1.110	1.108	4 ш	1.114	1.113	11 $\bar{2}$ 2
2 ш	1.088	1.090	2 ш	1.094	1.095	20 $\bar{2}$ 1

Параметры элементарной ячейки (Å)

$$a = 2.606 \pm 0.003 \qquad a = 2.617 \pm 0.002$$

$$c = 4.215 \pm 0.007 \qquad c = 4.226 \pm 0.004$$

Объем элементарной ячейки (Å³)

$$24.79 \pm 0.10 \qquad 25.06 \pm 0.06$$

Рентгеновская плотность (г/см³)

$$13.19 \qquad 13.80$$