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HERCYNITE-PLEONASTE FROM ILMENITE-MAGNETITE ROCKS OF KRZEMIANKA (NE POLAND)

UKD 549.731.11hercynit+549.731.11+546.72pleonast].08:553.311′494:552.311(438-18Krzemionka k. Suwałk)

A b s t r a c t. This paper describes green spinel containing 40—44 molar per cent of hercynite, occurring in ilmenite-magnetite rocks from Krzemianka (NE Poland). The results of optical, electron microscopic, X-ray, IR-spectroscopic, chemical and magnetic investigations of hercynite-pleonaste and synthetic hercynite are presented.

INTRODUCTION

Hercynite was first described in 1847 by Zippe (Strunz 1970) and named after the massif of Silva Hercynia in Bohemia (Lazarenko 1971). Hercynite $FeAl_2O_4$ and spinel $MgAl_2O_4$ belong to the commonest minerals in the spinel series. There is a continuous replacement series from hercynite to spinel. Hercynite with a considerable amount of Mg^{2+} replacing Fe^{2+}, with the Mg^{2+} to Fe^{2+} ratio ca. 3 : 1, is called pleonaste. In addition to the substitution of Fe^{2+} for Mg^{2+}, considerable Al^{3+}—Fe^{3+} substitution may occur, though there does not appear to be a complete natural series to magnetite. Continuous substitution of Cr^{3+} for Al^{3+} is also observed, there being a complete solid solution between hercynite and chromite (Deer et al. 1966).

In the minerals of the spinel group there are 32 oxygen ions and 24 cations in the unit cell (a=8.08—8.53 Å, Z=8), 8 of the cations in 4-fold coordination and 16 in 6-fold coordination.

Hercynite is commonly found in metamorphosed argillaceous sediments rich in iron, basic and ultrabasic igneous rocks, and also in some acid granulitic assemblages (Deer et al. 1966). The appearance, paragenesis and physico-chemical properties of hercynite from different deposits were described by Stewart (1942), Yamamoto (1958), Barth (1961), Fominykh and Yunikov (1961), Flinter (1963), Goroshnikov and Sizova (1963) et al. The occurrence of hercynite in ilmenite-magnetite deposits in NE Poland

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was ascertained by Juskowiak (1971), Kucha and Piestrzyński (1976) and Pilch et al. (1975).

The ilmenite-magnetite deposit located near Krzemianka (NE Poland) is associated with anorthositic and noritic rocks. Anorthosite and norite intruded into the Precambrian metamorphic massif consisting of gneiss, granite gneiss and granitoid rocks. The metamorphic rock with anorthosite-norite intrusions is covered by a Mesozoic-Kenozoic cap. Ilmenite-magnetite ore occurs as lenses (Makowski 1975). The ore contains magnetite, ilmenite, rock-forming silicates (mainly plagioclase and pyroxene with accessory biotite), pyrite, pyrrhotite, pentlandite, chalkopyrite and spinel minerals such as hercynite, pleonaste, ulvöspinel (Juskowiak 1971, Siemiątkowski and Kubicki 1974).

EXPERIMENTAL

The investigation was carried out on a sample containing 85.2% green minerals, 4.3% ilmenite and 10.5% anorthite (in volume %). The sample was separated from a hard rock ground below 0.25 mm (containing 0.3% hercynite) by a combination of flotation with sodium oleate, magnetic and gravity methods. To obtain comparative data, synthetic hercynite was used. $FeAl_2O_4$ was synthetized by mixing Fe, Fe_2O_3 and Al_2O_3 in the appropriate molar ratios. The powdered mixture was pressed into tablets, which were then placed in a corundum crucible and heated in a Mo crucible in an induction furnace. The synthesis procedure consists of three stages: 1 — degassing of the sample below 500°C, 2 — preliminary synthesis at 1200°C, and 3 — synthesis at 1750°C. The synthesis was performed at the International Laboratory of High Magnetic Fields and Low Temperatures, Wrocław, Poland, in Dr R. Horyń's laboratory.

For microscopic observation a thin section was prepared from a rock sample that was supplied by the Institute of Iron Metallurgy, Gliwice, Poland.

RESULTS

The anorthositic and noritic rocks taken from a borehole located in Krzemianka, NE Poland, contains (in vol.-%): plagioclase — 56.8, pyroxene — 17.0, ilmenite, magnetite, ulvöspinel, sulphide — 24.8, biotite — 1.0, green spinel — 0.3.

Mineralogical studies have shown that green spinel is closely associated with ilmenite and occasionally with magnetite and sulphides. Green spinel in ilmenite, a possible product of the decomposition of solid solution, is mostly oriented on *(100)* and occasionally on *(111)*. In thin section (Phot. 1), green spinel is observed in the form of: 1 — thin laminae inside ilmenite and magnetite and around these minerals, 2 — xenomorphic irregular grains about 0.05—0.8 mm in size, 3 — granular aggregates of small grains and sometimes in the form of octahedral crystals. The spinel studied has a black colour and sub-metallic lustre. In thin sections it is isotropic and has a green or dark green colour. It has a greyish-green streak and a conchoidal fracture. Octahedral parting along *(111)* may also

be observed (Phot. 2). The octahedral habit of spinel crystals is best seen on a scanning electron micrograph (Phot. 3). The characteristic feature of the investigated spinel is the presence of micro- and macro-defects and gas-liquid, ilmenite or sulphide inclusions. The ilmenite inclusions are often automorphic or irregular ilmenite crystals. The inclusions of sulphides are usually in the form of small pearl-drops. The refractive indices determined by immersion method using a solution of sulphur in methylene iodide is $n_{Na}=1.792$ (values determined for 12 grains). The specific gravity of green spinel at 20°C was determined by weighing the samples containing 85.2 green spinel, 4.3 ilmenite and 10.5 vol.-% of anorthite in air and then in ethyl alcohol. Taking into account that the specific gravity of the sample was 3.82 and s.g. of ilmenite is 4.72 and of anorthite 2.8, the s.g. of green spinel was estimated at 3.90.

CHEMICAL FORMULA OF GREEN SPINEL

Chemical analysis of the sample containing 86.9 wt.-% of green spinel has revealed 17.73% Fe, 11.05% MgO, 49.06% Al_2O_3, 4.39% SiO_2, 0.7% TiO_2, 0.0568% Ni, 0.0218% Ca, 0.14% Cr and 0.178% Zn. After the recalculation, the content of the main oxides in green spinel was found to be: 57.6% Al_2O_3, 14.05% MgO and 28.22% FeO. On the basis of this data, and assuming that iron is in the form of FeO, the chemical formula would be $(Mg_{0.47}Fe_{0.53})O \cdot 0.762\ Al_2O_3$. However, since a certain amount of iron is also in the from of Fe_2O_3, the formula for green spinel will be: $(Mg_{0.56}Fe^{2+}_{0.44})(Al_{1.81}Fe^{3+}_{0.19})O_4$. This is an approximate formula based on one chemical analysis only (only one 2 g sample was available), with the $Fe^{2+} : Fe^{3+}$ ratio not determined experimentally).

On the basis of the plot given by Deer at al. (1966, p. 431) and relating n, a_o and d with the composition of various portions of spinel minerals, the chemical formula of the studied spinel can also be estimated. For a specific gravity of 3.90 and a cell edge of 8.136 Å the formula is: $(Mg_{0.6}Fe^{2+}_{0.4})(Al_{1.9}Fe^{3+}_{0.1})O_4$, and for a specific gravity of 3.90 and the refractive index n=1.792, the formula is: $(Mg_{0.6}Fe^{2+}_{0.4})(Al_{1.85}Fe^{3+}_{0.15})O_4$. The combination of the refractive index and the cell edge gives a very low content of Fe^{2+} in green spinel. This suggests that the refractive index is likely to be underestimated.

The chemical formula of green spinel determined by chemical analysis and estimated from d and n values corresponds well to the formula $(Mg_{0.4-0.56}Fe^{2+}_{0.6-0.44})(Fe^{3+}_{0.11-0.06}Al_{1.89-1.94})O_4$ found by Kucha and Piestrzyński (1970) by microprobe analysis for green spinel from the Krzemianka deposit.

The intensity of X-ray K_α radiation generated by green spinel was recorded with the scanning microscope using an attachment for X-ray analysis. Introducing the „first approximation" equation $K=I_{Mg} : I_{Al}=C_{Mg} : C_{Al}$ (Philibert, Tixier 1969), where K is the molar ratio of the generated intensities (I) and C is the mass concentration of Mg and Al in the sample, the ratio of molar content of Al : Mg was found to be 3.42. Such approximation could be made due to the similarity of the atomic number of Mg (12) and Al (13). The value of 3.42 roughly confirms the formula of green spinel calculated from chemical analysis (Al : Mg molar ratio=3.23), from d and a_o values (Al : Mg molar ratio=3.2), and the formula determined by Kucha and Piestrzyński (1976), where the Al : Mg average ratio was 3.99.

IR ABSORPTION SPECTRA

The infrared absorption spectra of green spinel from Krzemianka and synthetic $FeAl_2O_4$ were recorded with a Specord 75 (Carl—Zeiss—Jena, GDR) spectrophotometer. KBr discs containing about 1 wt.% of the sample were used. The spectra of both samples in the wave-number range 400—1800 cm^{-1} are shown in Fig. 1. By analogy to $MgAl_2O_4$ and other normal cubic II—III spinels (Preudhomme, Tarte 1971) the two bands at 654 cm^{-1} (ν_1) and 497 cm^{-1} (ν_2) can be attributed to the lattice vibrations of AlO_6 octahedral groups. According to Preudhomme and Tarte, these frequencies are essentially determined by the nature (but not the mass) of the octahedral trivalent cations. The band below 400 cm^{-1} (ν_4) of $FeAl_2O_4$ and a weak but distinct shoulder at 557 cm^{-1} (ν_3) correspond to complex vibrations involving simultaneously the tetrahedral (FeO_4) and octahedral (AlO_6) groups. The absorption bands at 1600 and 3400—3600 cm^{-1} are caused by the surface molecular water.

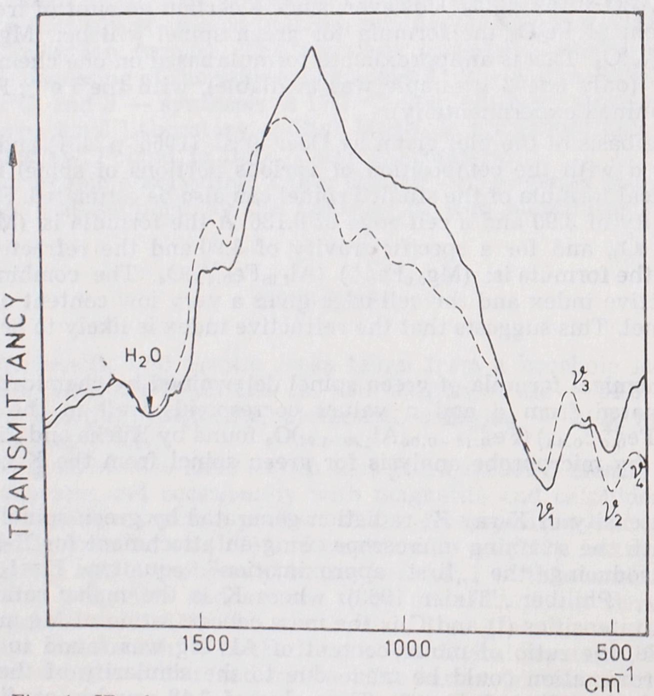

Fig. 1. IR absorption spectrum of hercynite-pleonaste from Krzemianka (dotted line) and synthetic hercynite (full line)

X-RAY STUDY

X-ray powder patterns were obtained with a DRON-1 diffractometer using CuK_α radiation. X-ray data for green spinel and $FeAl_2O_4$ are presented in Table 1. The recalculation of the X-ray diffraction pattern shows that the sample contains hercynite with a unit cell parameter of 8.136 ±0.005 Å. The sample also contains small amounts of ilmenite, magnetite and anorthite. The value of the cell edge of hercynite is in accordance with the data published by other authors, for example Kiryazova (1970), Renzberg (1967) and Feklikhev (1977). A peculiar feature of the green spinel is the lack of d_{440} reflection 1.440 Å.

X-ray specific gravity calculated for the cell edge 8.136 Å and the formulafor the unit cell: $(Mg_{4.48}Fe^{2+}_{3.52})\cdot(Al_{14.48}Fe^{3+}_{1.52})O_{32}$ estimated on the basis of chemical analysis is equal to 3.99, being consistent with the value 3.90 determined experimentally.

MAGNETIC SUSCEPTIBILITY

Magnetic susceptibility was determined using a Franz isodynamic magnetic separator and adopting the procedure described by Nesset and Finch (1980). It has been found that the relation between magnetic susceptibility and field strength H (in Oe) for green spinel is:

$$\varkappa_g = \frac{0.107}{H} + 17.25 \ 10^{-6} \text{ emu} \quad g^{-1} \ Oe^{-1}$$

Table 1

X-ray data for green spinel and synthetic hercynite

Green spinel				Synthetic hercynite			
d	*I*	mineral	a_o, Å	*d*	*I*	(*hkl*)	a_o, Å
4.687	1/2	hercynite (*111*)	8.1316	4.685	1/2	(*111*)	8.157
3.155	2	anorthite 3.118, I=10*					
2.865	4	hercynite (*220*)	8.1293	2.876	8	(*220*)	8.1523
2.710	1	ilmenite 2.74 I=10*					
2.516	2	magnetite 2.54 I=10*					
2.442	10	hercynite (*311*)	8.1130**	2.457	10	(*311*)	8.1575
2.029	4	hercynite (*400*)	8.1330	2.030	1	(*400*)	8.1369**
1.658	5	hercynite (*422*)	8.1396	1.662	1	(*422*)	8.1584
1.563	4	hercynite (*333*) or (*511*)	8.1364	1.567	5	(*333*) lub (*511*)	8.1581
—	—	—	—	1.440	10	(*440*)	8.1540
1.285	1	hercynite (*620*)	8.1419	1.285	1	(*620*)	8.1420
—	—	—	—	1.241	1/2	(*533*)	8.1585
1.058	1/2	hercynite (*731*)	8.1437	1.058	1/2	(*731*)	8.1569
Mean value 8.136±0.005***				Mean value 8.155±0.004***			

* — after Mikheev (1957).
** — values not taken into account for mean value calculation.
*** — mean value at 95% confidence level.

CONCLUSIONS

It has been estimated that the formula for the green spinel from the ilmenite-magnetite ore from Krzemianka (NE Poland) is $(Mg_{0.56}Fe^{2+}_{0.44})(Al_{1.81}Fe^{3+}_{0.19})O_4$. The $Mg : Fe^{2+}$ ratio in this spinel is about 1.3. Thus the spinel under examination contains as much Mg as pleonaste or ceylonite, in which the $Mg : Mg^{2+}$ ratio varies from 3 to 1 (Deer et al. 1966), and contains about 44 molar % of hercynite. It has also been found that a certain amount of trivalent iron substitutes for Al in the spinel lattice. Therefore the green spinel from Krzemianka is hercynite-pleonaste from the continuous series spinel $MgAl_2O_4$—hercynite $Fe^{2+}Al_2O_4$—magnesioferrite $MgFe^{3+}_2O_4$—magnetite $Fe^{2+}Fe^{3+}_2O_4$.

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HERCYNITO-PLEONAST ZE SKAŁ ILMENITOWO-MAGNETYTOWYCH Z KRZEMIANKI (NE POLSKA)

Streszczenie

Przedstawiono wyniki badań mikroskopowych, rentgenowskich, spektroskopowych w podczerwieni oraz chemicznych zielonego spinelu ze skał ilmenitowo-magnetytowych z Krzemianki (północno-wschodnia Polska). Badania przeprowadzono używając próbki zawierającej 85,2 obj.% zielonego spinelu, 4,3 obj.% ilmenitu i 10,5 obj.% skaleni. Próbkę wydzielono ze zmielonej rudy ilmenitowo-magnetytowej zawierającej około 3% spinelu przez flotację z olejanem sodu a następnie przez seperację magnetyczną i seperację grawitacyjną. Stwierdzono, że spinel ten o przybliżonym wzorze $(Mg_{0,56}Fe^{2+}_{0,44})(Al_{1,84}Fe^{3+}_{0,19})O_4$ pochodzi z szeregu izmorficznego spinel $(MgAl_2O_4)$—hercynit $(Fe^{2+}Al_2O_4)$—magnezoferryt $(MgFe^{3+}_2O_4)$—magnetyt $(Fe^{2+}Fe^{3+}_2O_4)$ i zawiera 44% mol. hercynitu. Badany hercynito-pleonast jest czarny o połysku półmetalicznym, w cienkich płytkach zielony i posiada zielonoszarą rysę a przełam muszlowy. Gęstość jego wynosi 3,90 g/cm^3, gęstość rentgenograficzna 3,99 g/cm^3. Pozostałe dane: stała sieciowa $a_o = 8{,}136 \pm 0{,}005$ Å, pasma absorpcyjne w podczerwieni 654 (ν_1), 497 (ν_2), 557 (ν_3 i poniżej 400 cm^{-1} (ν_4). Główne refleksy rentgenowskie 2,865 (4), 2,442 (10), 2,02 (4), 1,658 (5), 1,563 (4). Współczynnik załamania światła $n_{Na} = 1{,}792$. Podatność magnetyczna $\varkappa_g = 0{,}107/H + 17{,}25\ 10^{-6}$ j.em. g^{-1} Oe^{-1}, gdzie H jest natężeniem pola magnetycznego w Oe.

OBJAŚNIENIE FIGURY

Fig. 1. Widmo absorpcyjne w podczerwieni hercynito-pleonastu z Krzemianki (linia przerywana) i syntetycznego hercynitu (linia ciągła).

OBJAŚNIENIA FOTOGRAFII

Fot. 1. Hercynito-pleonast ze skał ilmenitowo-magnetytowych z Krzemianki (w kółkach). Pow. 70×

Foto. 2. Hercynito-pleonast. Przełam muszlowy, oktaedryczna łupliwość według *(111)*. Pow. 300×

Foto. 3. Hercynito-pleonast. Oktaedryczny pokrój kryształu. Pow. 900×

ГЕРЦИНИТ-ПЛЕОНАСТ В ИЛЬМЕНИТ-МАГНЕТИТОВОЙ ПОРОДЕ ИЗ КШЕМЯНКИ, (СЕВЕРО-ВОСТОЧНАЯ ПОЛЬША)

Резюме

В работе представлены результаты микроскопических, рентгеновских ИК-спектроскопических, магнитных и химических исследований зеленой шпинели из ильменит-магнетитовой породы из Кшемянки. Путем флотации, гравитационной и магнитной сепарации удалось получить образец зеленой шпинели, содержащий 85,2% зеленой шпинели, 4,3% ильменита и 10,5% полевых шпатов (в объемных %). Доказано, что изучаемая шпинель это герцинит-плеонаст $Mg_{0,56}Fe^{2+}_{0,44}Al_{1,84}Fe^{3+}_{0,1904}$ ряда шпинель ($MgAl_2O_4$)—герцинит ($Fe^{2+}Al_2O_4$)—магнезиоферрит ($MgFe^{3+}_2O_4$)—магнетит ($Fe^{2+}Fe^{3+}_2O_4$). Минерал черного цвета. В прозрачных шлифах зеленый, излом раковистый, черта зеленого или зелено-серого цвета, блеск полуметаллический, плотность 3,99; размер элементарной ячейки $a_o = 8.136 \pm 0.005$. Главные линии на рентгенограммах: 2.865 (4), 2.44 (10), 2.029 (4), 1.658 (5), 1.563 (4). Показатель преломления $n = 1.792$. Главные плолосы на инфракрасном спектре поглощения $\nu_1 = 654$, $\nu_2 = 497$, $\nu_3 = 557$, $\nu_4 =$ ниже 400 $см^{-1}$. Магнитная восприимчивость $\chi_g = \frac{0,107}{H} 17.25.10^{-6}$ (H = напряжение магнитного поля в Э.).

ОБЪЯСНЕНИЕ К ФИГУРЕ

Фиг. 1. ИК-спектр поглощения герцинит-плеонаста из Кшемянки (прерывистая линия) и синтетического герцинита (сплошная линия).

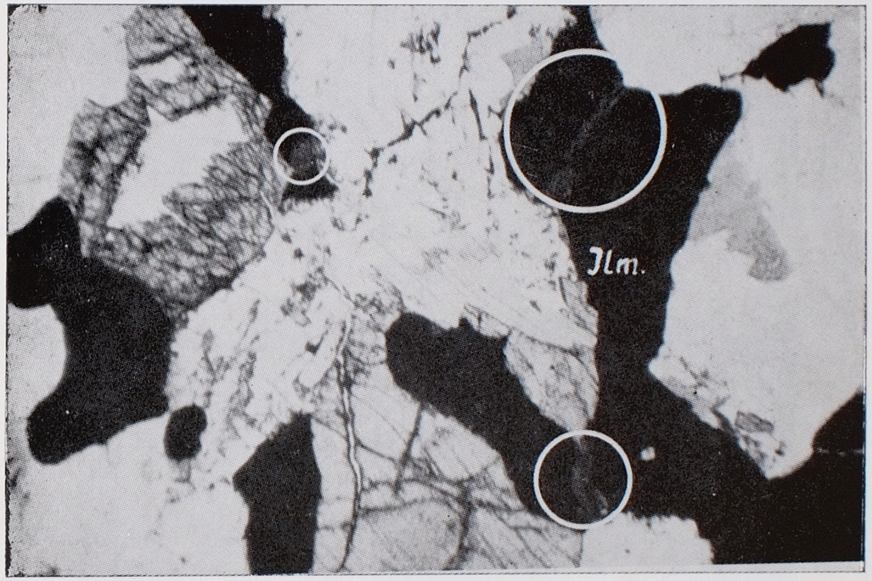
ОБЪЯСНЕНИЯ К ФОТОГРАФИЯМ

Фото 1. Герцинит-плеонаст в ильменит-магнетитовой породе из Кшемянки. Увел. 70 ×

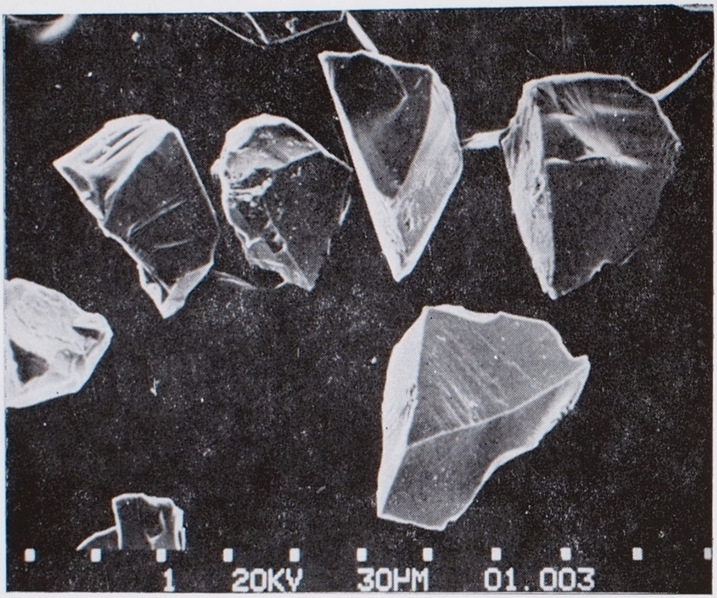
Фото 2. Герцинит-плеонаст. Раковистый излом и октаэдрический габитус (*111*), редко. Увел. 300 ×

Фото 3. Герцинит-плеонаст. Октаэдрический габитус. Увел. 900 ×

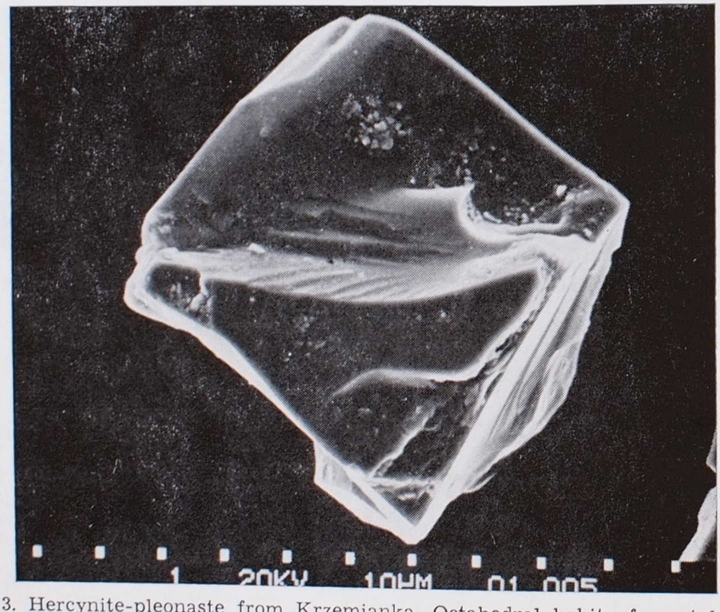
Москва.



Phot. 1. Hercynite-pleonaste in ilmenite-magnetite rocks from Krzemianka (in circles). Magn. 70×



Phot. 2. Hercynite-pleonaste from Krzemianka. Conchoidal fracture, octahedral parting along (*111*). Magn. 300×



Phot. 3. Hercynite-pleonaste from Krzemianka. Octahedral habit of crystal. Magn. 900×

Jan DRZYMAŁA, Andrzej ŁUSZCZKIEWICZ, Piotr SIMICZYJEW — Hercynite-pleonaste from ilmenite-magnetite rocks of Krzemianka (NE Poland)