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OCCURRENCE OF HOROBETSUITE $(Bi, Sb)_2S_3$ AT THE DEPOSIT DÚBRAVA

(Figs. 1—13)

Abstract: In the frame of mineralogical-geochemical investigation of antimonite mineralization of the Nízke Tatry Mts. minerals of the bismutite-antimonite order not described by us have been found at the deposit Dúbrava. Minerals of the isomorphous order bismutite-antimonite are present very rarely under natural conditions. For this reason many of them are very little studied. So far as the middle member of the bismutite-antimonite order has been known horobetsuite (K. Hayase 1955) and bismutite with higher Sb-content (G. Springer 1969).

Резюме: Во время минералогического — геохимического исследования антимонитовой минерализации Низких Татр, было обнаружено на месторождении Дубрава несколько, у нас неописанных минералов висмутиново — антимоинтового порядка. Минералы изоморфного порядка висмутин — антимонит в естественных условиях находятся очень редко. По этой причине почти все минералы данного порядка изучены очень недостаточно. До сих пор известен средний член вышеупоминаемого порядка — горобетсуит (К. Гаясе 1955) и висмутин с более высоким содержанием Sb (Г. Спрингер 1969).

At the deposit Horobetsu (K. Yagi 1958) horobetsuite is found in the shape of prismatic, vertically striated crystals. Specific gravity at 20° C is 5,449. The colour is steel-grey, the streak black, it is anisotropic with pale-yellow, grey and dark-brown shade. The values of crystal lattice are: $a_0 = 11.24$ $b_0 = 11.28$ $c_0 = 3.90$. Diagnostic etching by reagents in standard concentration: HNO_3, HCl, $HgCl_2$, $FeCl_3$ — brownish-black spots, KOH 9—300 sec. brown spots, KCN 35—85 sec. brown spots. The chemical formula on the basis of three analyses was determined by K. Hayase (1955) as $(Bi, Sb)_2S_3$. The molar ratio $Bi_2S_3 : Sb_2S_3$ was between 9:11 to 13:7. At last he remarks that the name horobetsuite he suggests for a mineral of the bismutite-antimonite order from various world deposits, quotes that substitution of bismuth by basis of the mentioned description horobetsuite was recognized as a new mineral by an international commission (K. Yagi 1958).

G. Springer (1969), based on about 70 analyses of minerals of the bismutite-antimonite order from various world deposits quotes that substitution of bismuth by antimony can occur up to 42 mol. % Sb_2S_3. For such natural occurrences of solid solution $Bi_2S_3 — Sb_2S_3$ he uses the designation bismutinite. He considers horobetsuite as a Sb-rich, terminal member in natural occurrence of solid solution $Bi_2S_3 — Sb_2S_3$. K. Hayase (1955) proved by chemical analyses the solid soluble solution $Bi_2S_3 — Sb_2S_3$ up to 55 molar % Sb_2S_3. Accordingly also G. Springer mentions that the limit of miscible orders lies in the composition $(Bi_{0,45}Sb_{0,55})_2S_3$. He remarks that minerals with chemical composition between horobetsuite and antimonite were not found in nature although such minerals were obtained artificially.

Minerals of the bismutite-antimonite order (bismutite, horobetsuite, antimonite)

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belong to one structural type (rhomb. s.) in the mineralogical system. The end members of the order differ from one another in physical-chemical properties as well as in different conditions of origin. Bismutite is more often found at higher- and/or medium-thermal deposits. Antimonite, on the contrary, is known from low- and medium-thermal deposits. The rare occurrence of horobetsuite, deficiency of experimental data about the Bi-Sb-S system, different conditions, of the origin of end members of the order point to very specific conditions of formation of this mineral. It has been proved by experimental study of the Bi-Sb system (F. V. Čuchrov 1960) that from the solid solution Bi-Sb a continuous order of isomorphous mixtures can form, stable also at low temperatures. With the assumption of continuous isomorphism in the order bismutite-antimonite (isomorphism in this order to 42 mol. % Sb_2S_3 was proved by G. Springer) and on the basis of performed study (K. Hayase, G. Springer) and of own results we suggest a division of the isomorphous order as follows:

		mol. %	
100	Bi_2S_3	0	bismutite
75		25	
			horobetsuite
25		75	
0	Sb_2S_3	100	antimonite

The division of the isomorphous order into three members with the limits 0—25, 25—75, 75—100 is common also at other isomorphous orders. To this division of the order with shifted limits (25, 75) in contrast to the division suggested by K. Hayase (30, 70) suit better the results of our observation as well as the results of G. Springer. In the diagram of the bismutite-antimonite order constructed by G. Springer (1969) on the basis of carried out analyses, is clearly separated the field of more frequently occurring minerals with the content of up to 25 mol. % Sb_2S_3 from the field of rare minerals with the content of more than 25 mol. % Sb_2S_3. The three studied cases of minerals of the bismutite-antimonite order belong to horobetsuite according to chemical composition and the suggested division of the isomorphous order.

The samples studied were taken from the exploited deposit Dúbrava. The deposit belongs to the antimonite formation of the Nízke Tatry with distinct stockwork character. It extends 4 km long, in its whole extent a general veiny structure striking N—S is evident, of which the individual segments in various tectonic blocks were given various names (deposit sections). The main ore mineral is antimonite while other minerals — hematite, pyrite, arsenopyrite, sphalerite, tetrahedrite, chalcopyrite, chalcostibite, bournonite, boulangerite, zinkenite, native Au, Sb, molybdenite, scheelite— are subordinately to accessorily represented.

From nonmetallic minerals quartz predominates over carbonates (Fe-dolomite, siderite, calcite) and barite.

In two cases the properties of horobetsuite found at the veins Elena and Bielopotocká diference is only in the presence of Cu (thus also in the lower Sb-content) in sample 1, in the shape of own grains 0.1—0.4 mm in size, of elongated and isometric shape in chalcostibite, rarely in tetrahedrite (fig. 1, 2). In reflected light it is yellowish-white. Reflectance is higher than in antimonite. Double reflection is weak, greyish-white in direction of elongation, yellowish-white perpendicular to elongation. It is anisotropic in greyish-white, greyish-brown and brown colour shades. Diagnostic etching by

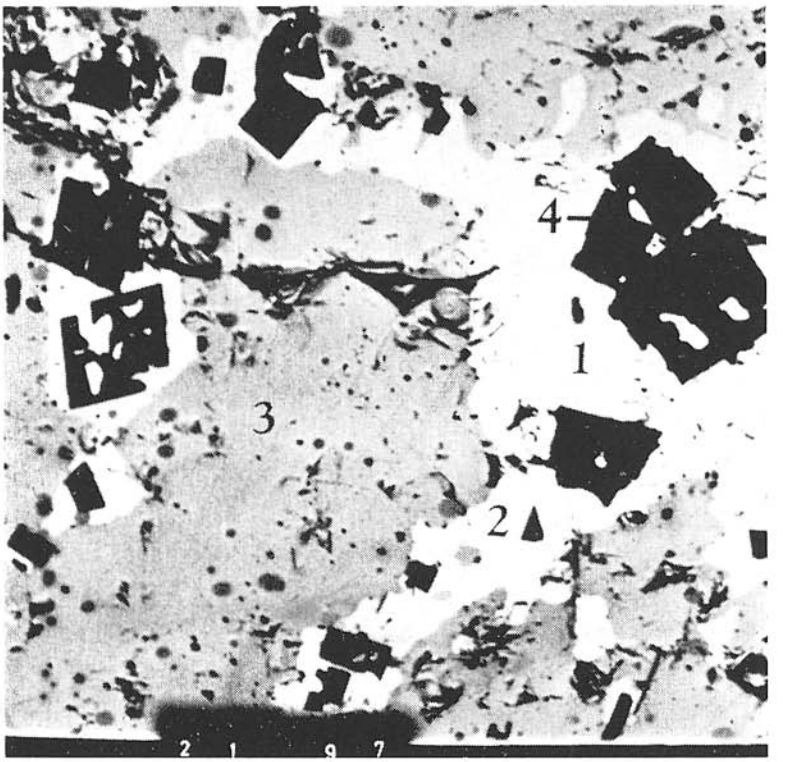

Fig. 1. Composition. 1 — Horobetsuite, 2 — chalcostibite, 3 — tetrahedrite, 4 — pyrite. Magnif. 300 ×. Sample no. 2.

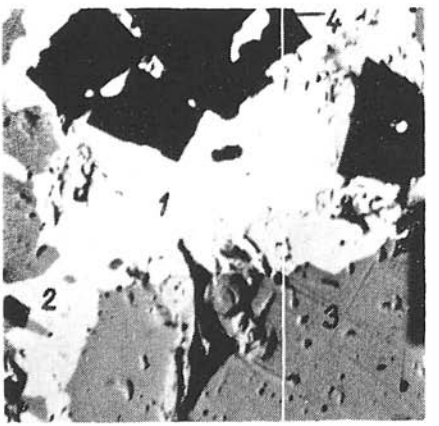

Fig. 2. Composition. The same as fig. 1. Magnif. 600 ×. Sample no. 2.

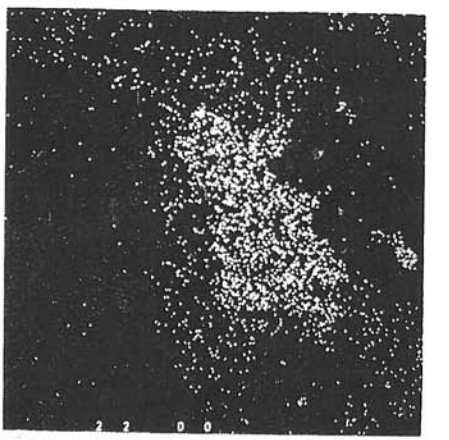

Fig. 3. Distribution of BiMα. Magnif. 600 ×.

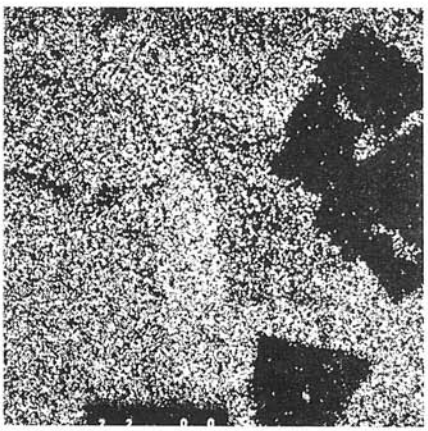

Fig. 4. Distribution of SbLα. Magnif. 600 ×.

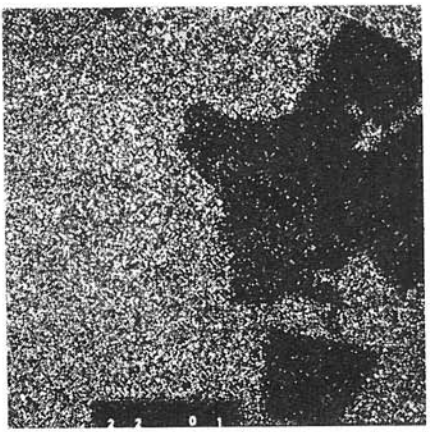

Fig. 5. Distribution of CuKα. Magnif. 600 ×.

reagents in standard concentrations provided the following results: HNO_3 — is quickly getting brown, later black, HCl — brown, later black coating. $HgCl_2$ — slowly a pale-brown, dull surface forms. $FeCl_3$, KOH, KCN — not acting.

Microhardness measured on microhardness-meter PMT-3 (arrestment 15 s., exposure 10 s. 20 measurements on one sample) with weight 10 gr. is $H_{max} = 138.6$ kg/mm^2. $H_{min} = 93.4$ kg/mm^2. $H_{mean} = 114.6$ kg/mm^2.

The determined optical properties agree with the mentioned properties of horobetsuite from Japan (K. Hayase 1955). Differences have been found only in the results of diagnostic etching (reagents $FeCl_3$, KCN do not act on horobetsuite from Dúbrava).

Chemical composition was studied on X-ray microanalyser JXA-5A by J. Krištín. By means of quantitative analysis the presence of Bi, Sb, Cu, S has been established. The concentration curves and X-ray diffraction patterns of distribution of individual elements (fig. 3—11) have confirmed an equable distribution of the present elements.

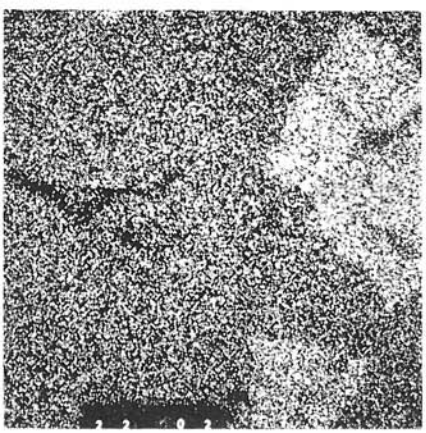

Fig. 6. Distribution of SKα. Magnif. 600 ×.

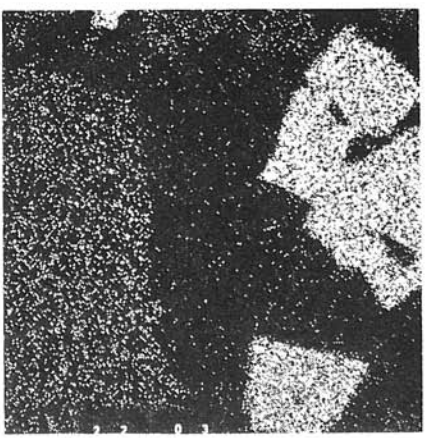

Fig. 7. Distribution of FeKα. Magnif. 600 ×.

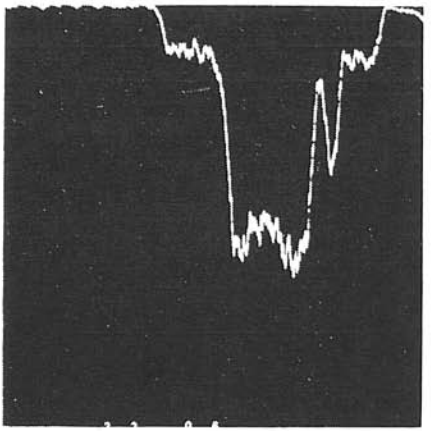

Fig. 8. Line analysis of BiMα. Magnif. 600 ×.

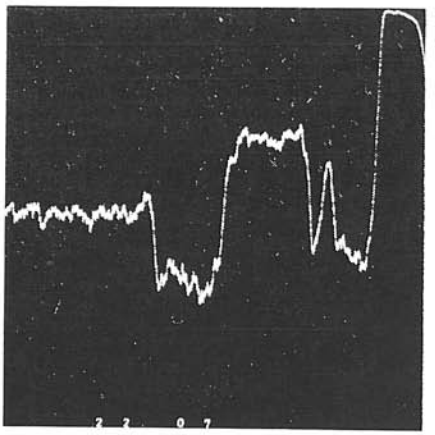

Fig. 9. Line analysis of SbLα. Magnif. 600 ×.

Quantitative analyses were carried out with a current of 25 kV. As standards were used: Sb — Sb_2S_3. Bi — Bi_2S_3. (Bi). Cu — $CuFeS_2$. S — Bi_2S_3. (Sb_2S_3). The average analysis was calculated from three point analyses of the individual mineral grains. In recalculation of analyses according to the programme SONDA 03 on computer CDC 3300 were used corrections to: absorption, dead running of detector, atomic number, fluorescence and exit angle.

With recalculation of analyses (tab. 1) we obtained the formulas $(Bi_{1,21}Sb_{0,65})_{1,86}Cu_{0,12}{}_{1,98}S_3$. Chemical composition of the analysed minerals is very close. The difference is only in the presence of Cu (thus also in the lower Sb-content) in sample 1. The molar ratio $Bi_2S_3 : Sb_2S_3$ in sample 1 is 6,5:3,5, in sample 2 is 6,4:3,6. On the basis of calculated molar ratios $Bi_2S_3 : Sb_2S_3$ and according to the mentioned division of the isomorphous order we may consider both the minerals as horobetsuite.

The third observed sample with horobetsuite present (tab. 2) comes from recently mined short veins in the deposit section Ľubelská at the lower Ignác adit. The vein

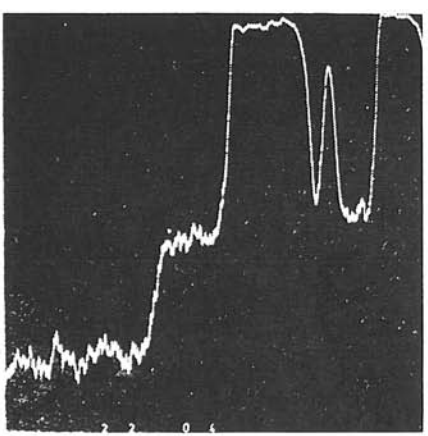

Fig. 10. Line analysis of CuKα. Magnif. 600 ×.

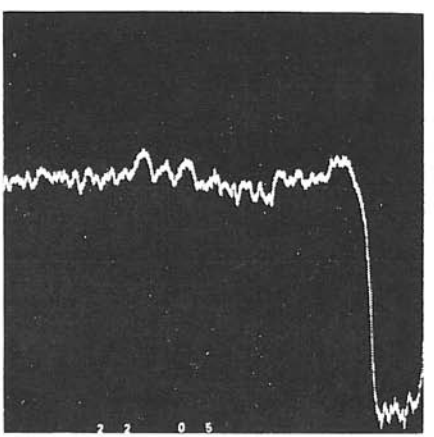

Fig. 11. Line analysis of SKα. Magnif. 600 ×.

Table 1. Average analyses and their recalculation

	Sample 1			Sample 2		
	Weight %	Atomic amount	Sample coeff.	Weight %	Atomic amount	Sample coeff.
Bi	58,2	0,2784	1,21	58,1	0,2779	1,21
Sb	18,2	0,1494	0,65	19,1	0,1568	0,68
Cu	1,8	0,0283	0,12	0,0	—	—
S	22,3	0,6947	3,00	22,1	0,6884	3,00
Σ	100,5			99,3		

Sample 1 — Dúbrava—Predpekelná, Elena vein, main haulage rock crosscut
Sample 2 — Dúbrava—Dechtárka, vein Bielopotocká Underlying, Bielopotocká II. adit

infilling is formed by coarse-grained- to rodlike chalcostibite, fine-grained barite, rare tetrahedrite and pyrite. Microscopically have been found horobetsuite and chalcopyrite in isolated cases. Horobetsuite is found in the shape of irregular to elongated individuals (fig. 12), granular aggregates less than 0,1 mm in size in chalcostibite in close proximity to strongly replaced tetrahedrite. When compared with chalcostibite it has a higher reflectance. Double reflection is clear, well observable on aggregates. In the direction of elongation it is white with cream shade, perpendicular to elongation pale-grey. It is highly anisotropic, with yellowish-brown, creamlike, greyish-brown to black colouring. Etching test: HNO_3 — causes slow browning, later black colour, HCl — slow reaction, weak browning, KOH — grey, at the margin of grains black coating. $HgCl_2$, $FeCl_3$, KCN — not acting. The small dimensions did not permit to employ further identification methods.

With recalculation of the analysis we have obtained the formula $(Sb_{1,38}Bi_{0,48})_{1,86}Cu_{0,08}$ $_{1,94}S_3$. As visible from the chemical analysis and recalculation, the ratio $Bi_2S_3 : Sb_2S_3$ — 2,6:7,4 is contrary than in the foregoing two samples. This ratio in favour of Sb_2S_3 is still higher (fig. 13) than proved by K. Hayase (1955). Similarly as in the foregoing two cases also this mineral we may consider as horobetsuite on the basis of recalculation of the analysis and of the mentioned division of isomorphous order.

When comparing the results of diagnostic etching of the studied horobetsuite with bismutite and antimonite (tab. 3) we see a conspicuous accordance of etching properties

Table 2. Average analysis with recalculation

	Weight %	Atomic amount	Sample coeff.
Bi	27,42	0,1312	0,48
Sb	45,30	0,3720	1,38
Cu	1,38	0,0217	0,08
S	25,90	0,8078	3,00
Σ	100,00		

Sample 3 — Dúbrava—Ľubelská, lower Ignác adit, heading S-7

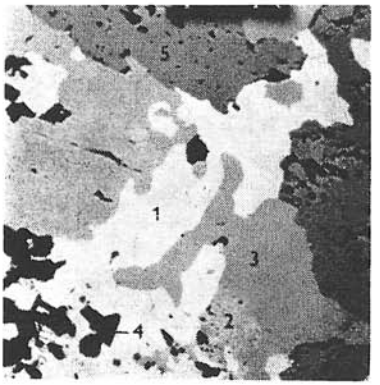

Fig. 12. Composition. 1 — Horobetsuite, 2 — chalcostibite, 3 — tetrahedrite, 4 — pyrite, 5 — barite. Magnif. 600 ×. Sample no. 3.

between bismutite and horobetsuite 1,2, and antimonite and horobetsuite 3. Regarding to the microscopic dimensions and the influence of surrounding environment (chalcostibite), the results of diagnostic etching (mainly in horobetsuite 3) are not quite convincing. The measured microhardness of horobetsuite (tab. 3) corresponds well to a member in the order bismutite-antimonite.

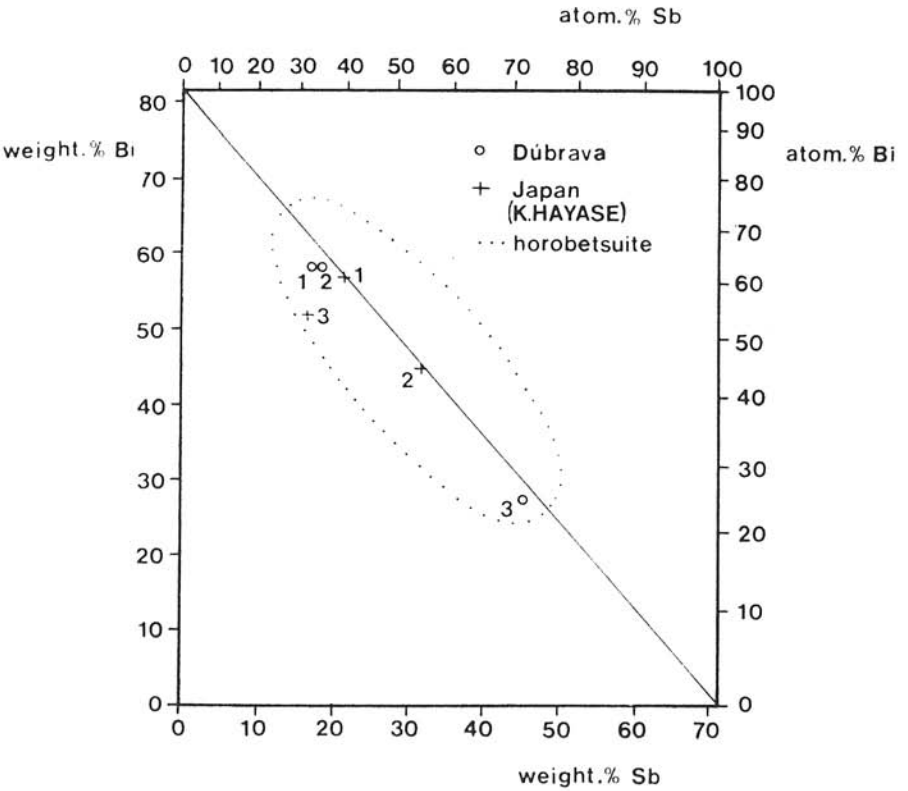

Fig. 13. Diagram of bismutite-antimonite order.

Table 3. Comparison of diagnostic etching and microhardness in bismutite-antimonite order

BISMUTITE		HOROBETSUITE		ANTIMONITE
		Sample 1, 2	Sample 3	
HNO_3	+	+		+
HCl	+	+	+	+
$HgCl_2$	+	+	–	–
$FeCl_3$	–	–	–	–
KOH	–	–	+	+
KCN	–	–	–	+
H	118–172+	93–139++		51–125 kg/mm²++

+– I. I. Lebedev (1963), ++– author, Dúbrava deposit

The described horobetsuite was forming in the main sulphidic stage (J. Hak 1966), in the stage of formation of copper sulphides (tetrahedrite, chalcostibite, bournonite). Within the observed association precipitation of horobetsuite took place only after tetrahedrite and chalcostibite formed. The succession tetrahedrite-chalcostibite-horobetsuite is also pointed out by the chemical composition of chalcostibite of the third studied sample. When comparing chemical composition of horobetsuite (tab. 2) with chalcostibite (Sb–45,89 Bi–2,14 Cu–26,31 S–25,51) we see that the contents of Sb and S do not change in these minerals and the contents of Cu and Bi are contrary.

Translated by J. PEVNÝ.

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Review by M. KODĚRA.