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ON THE CHEMICAL COMPOSITION OF GERMANITE

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Germanite is a very rare mineral that commonly occurs as small segregations in association with bornite, renierite, fahlores, sphalerite, galena, and other sulfides and sulfosalts. Very fine structures of replacement of germanite for renierite are often observed. Such small segregations are difficult to study. Optical properties of germanite are slightly variable in different areas and in samples from different deposits. The chemical composition (concentrations of the principal elements) of germanite varies over a wide range. In addition, the mineral was revealed to contain a wide set of admixtures. Therefore, different researchers propose different formulas for germanite. Chemical and electron microprobe analyses of germanite, accessible in literature, were compiled by the author, and peculiarities of the chemical composition of germanite were studied. It has been revealed that 28 analyses from 37 ones are adequately recalculated to the formula with 66 atoms in the unit cell; 6 analyses, to the formula with 64 atoms; and 3 analyses, with 68 atoms. The Me/S ratio in the analyses varies from 32:32 to 34:32 and to 36:32; that is, this ratio in the real analyses is inconstant. This fact suggests that we deal either with solid solutions or with three different, but similar in the chemical composition and properties, minerals. The second assumption is more probable. It is concluded that there exist three mineral species close to germanite in the chemical composition.
8 tables, 3 figures and 22 references

Germanite has been known from the 1920s. It was discovered by G. Schneiderhцhn (1920) at the Tsumeb ore deposit, Namibia, and was described and named so by O. Pufahl (1920). Later, the mineral was found at the Bancairoun, France (Levy, 1966) and Radka, Bulgaria (Kovalenker, *et al.,* 1986) ore deposits. Finds of complex Ge sulfides were reported from some Russian ore deposits, including the Pai-Khoi, Urup, Gai, III International, and Kurumsak ones, and from the Chelopech ore deposit, Bulgaria. However, these minerals contained large concentrations of either As or V, or, sometimes, of As and V together. In this case, concentrations of these elements were comparable with that of Ge and sometimes exceeded it. We excluded these analyses from the consideration, because they were probably assigned to germanocolusite or colusite.

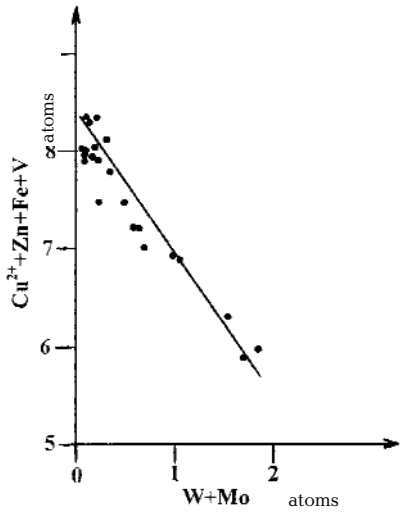

***Fig. 1**. Dependence between $Cu^{2+} + Fe + Zn$ and $W + Mo$ in analyses of germanite*

At all the ore deposits, germanite is associated with bornite, renierite, fahlores, and galena, being commonly intimately intergrown with these minerals. Very fine structures of replacement of germanite for renierite are often observed. Such small segregations are difficult to study. Optical properties of germanite are slightly variable in different areas and in samples from different deposits. Its color under reflected light is pink with violet tint, being very unequal. According to the optical features, L. Loginova (1960) distinguished three individual varieties of germanite.

The chemical composition (concentrations of the principal elements) of germanite varies over a wide range (in wt.%): Cu 40.9—51.0, Fe 0.0—10.7, Ge 3.0—11.0, Zn 0.0—5.5, and S 30.0—34.5. In addition, the mineral was revealed to contain a wide set of admixtures, including As, V, Ga, Sn, Sb, W, Mo, Pb, and Ag. Therefore, different researchers propose different formulas for germanite (Tables 1 and 2). These formulas are characterized by different cation/anion ratios equal to 1 : 1 (Sclar *et al.*,1957; Levy, 1966); 1 : 0.95 = 1.052 (Springer, 1969); 34 : 32 = 1.062 (Tettenhorst and Corbato, 1984; Spiridonov, 1987; Godovikov, 1997); and 36 : 32 = 1.125 (Spiridonov *et al.*, 1992).

Table 1. **Germanite formulae proposed by different researchers**

Formula	Reference	Me/S
$Cu_3(Fe,Ge)S_4$	De Jong, 1930	1
$Cu_3(Fe,Ge,Zn,Ga)(S,As)_4$	Sclar *et al.*, 1957	1
$Cu_6FeGeS_8 \rightarrow Cu^{+}{}_3Cu^{2+}{}_3Fe^{3+}Ge^{4+}S_8$	Levy, 1966	1
$(Cu,Fe,Zn,W,Mo,V,Ge,As\ Ga)S_{0.95}$	Springer, 1969	1.052
$Cu_{26}Fe_4Ge_4S_{32} \rightarrow Cu^{+}{}_{16}Cu^{2+}{}_{10}Fe^{3+}{}_4Ge^{4+}{}_4S_{32}$	Tettenhorst *et al.*, 1984	1.062
$Cu^{+}{}_{20}(Cu^{2+},Fe^{2+},Zn)_6Fe^{3+}{}_2Ge_6S_{32}$	Spiridonov, 1987	1.062
$Cu^{+}{}_{22}(Cu^{2+},Fe^{2+},Zn)_6Fe^{3+}{}_2(Ge,As)_6S_{32}Cu^{+}{}_{22}(Cu^{2+}{}_2Fe^{2+}{}_2Zn_2)_6Fe^{3+}{}_2(Ge_4As_2)_6S_{32}$	Spiridonov *et al.*,, 1992	1.125
$Cu^{+}{}_8Cu^{2+}{}_5Fe^{3+}{}_2Ge^{4+}{}_2S_{16}$	Godovikov, 1997	1.062

Table 2. **Theoretical composition of germanite (in wt. %), based on formulae proposed by different researchers**

Authors	Cu	Cu^+	Cu^{2+}	Fe	Zn	Ge	As	S
Levy, 1966	49.76	24.88	24.88	7.29		9.47		33.48
Tettenhorst, Corbato, 1984	51.76	31.85	19.91	7.00		9.1		32.14
Spiridonov, 1987	43.50	39.55	3.95	6.95	4.07	13.55		31.93
Spiridonov, 1992	45.58	41.78	3.80	6.68	3.91	8.68	4.48	30.67
Godovikov,1997	51.76	31.85	19.91	7.00		9.1		32.14

The crystal structure of germanite is derivative from the crystal structure of sphalerite and is close to those of stannite and colusite. Based on this fact, R. Tettenhorst and C. Corbato (1984) proposed a formula of germanite, similar to that of colusite, namely $Cu_{26}Fe_4Ge_4S_{32}$. This formula is electrically neutral only on condition that it contains 10 atoms of divalent Cu and 4 atoms of trivalent Fe. The presence of 10 atoms of divalent Cu is also specified by a crystallochemical formula of germanite, proposed by A. Godovikov (1997), $Cu^{+}{}_8Cu^{2+}{}_5Fe^{3+}{}_2Ge^{4+}{}_2S_{16} \rightarrow Cu^{+}{}_{16}Cu^{2+}{}_{10}Fe^{3+}{}_4Ge^{4+}{}_4S_{32}$. A crystallochemical formula of germanite, proposed by E. Spiridonov (1987), $Cu^{+}{}_{20}(Cu^{2+},Fe^{2+},Zn)_6Fe^{3+}{}_2Ge^{4+}{}_6S_{32}$, is not electrically neutral. Later, in the work on germanocolusite, E. Spiridonov with co-authors (1992) proposed another crystallochamical formula for germanite, $Cu^{+}{}_{22}(Cu^{2+},Fe^{2+},Zn)_6Fe^{3+}{}_2(Ge,As)_6S_{32}$. In this case, the formula is electrically neutral, but the sum of atoms in the unit cell is 68 rather than 66 as in colusite whose formula was adopted by E. Spiridonov as the basis for examination of the germanite formula; therefore, the Me/S ratio is equal to 36/32 rather than 34/32.

These contradictions prompted us to make an additional analysis of the literature data on germanite.

37 chemical and electron microprobe analyses of germanite were found and recalculated into formulae with regard to necessity of their electrical neutrality (Table 3 and 4). A formula was considered to be electrical neutral if it had the valence balance ($\pm\Delta$, the absolute value of the deviation from zero) no higher than 3%. To calculate the valence balance, it was necessary to understand the positions of admixtures in the crystal structure.

The p-elements, Ge, As, and Ga, are the neighbors in Mendeleev's Periodic Table and have similar electronic structures, therefore, they can be isomorphous. Other admixtures, V, Fe, Cu, Mo, and W are d-elements; so, it can be assumed that V, Mo, and W can substitute Fe and Cu, occupying the sites of divalent cations or trivalent Fe. The sum (W + Mo) depends inversely on the sum (Cu^{2+} + Fe + Zn), which evidences in favor of the assumption that W and Mo occupy the sites of divalent cations or trivalent Fe (Fig. 1). The sum (Cu + As) inversely proportional to the sum (Zn + Ge), which is evidence for the isomorphism $Zn^{2+} + Ge^{4+} \rightarrow Cu^{+} + As^{5+}$ (Fig. 2).

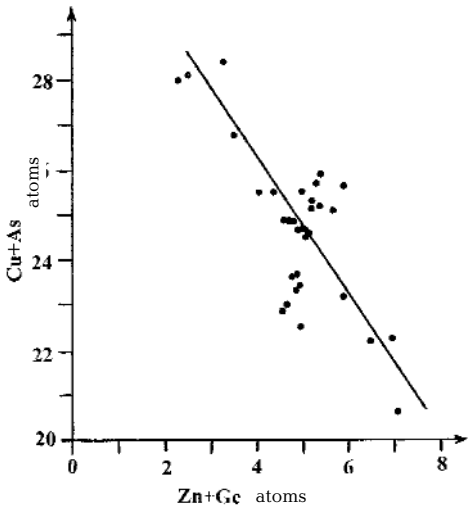

Fig. 2. *Dependence between Cu + As and Zn + Ge in analyses of germanite*

Table 3. **Electron microprobe and chemical (•) analyses of germanite in wt. % (upper row) and in f.u. (lower row). Analyses 1, 6, 22, 23, 24, and 36 are recalculated based on 64 atoms in the unit cell; analyses 8, 21, and 35, based on 68 atoms; the remainder, based on 66 atoms**

№ os.	Cu	Fe	Zn	Ge	Ga	As	V	W	Mo	S	Σ
1	45.1	7.4	1.3	9.7	0.00	2.6				33.4	99.5
	21.92	4.09	0.61	4.13		1.07				32.17	63.99
2•	45.4	7.22	2.61	6.20		5.03				31.34	99.246
	23.38	4.23	1.31	2.79		2.20				31.98	66.00
3•	42.12	7.80	3.93	10.2	1.85	1.37				31.27	99.49
	21.57	4.55	1.96	4.57	0.86	0.60				31.74	66.00
4•	45.39	4.56	2.58	8.70		4.13				30.65	99.55
	23.98	2.74	1.32	4.02		1.85				32.09	66.00
5•	39.44	10.7	3.56	7.04		4.86				31.44	99.98
	20.38	6.29	1.79	3.18		2.13				32.19	66.00
6	44.20	6.70	1.50	9.70		3.30				34.60	100.0
	21.25	3.66	0.70	4.08		1.35				32.96	64.00
7	46.5	8.5		9.4		4.2				31.6	100.26
	23.50	4.89		4.16		1.80				31.65	66.00
8•	43.6	6.4	3.10	9.0		4.70				30.03	97.7
	23.67	3.95	1.64	4.28		2.16				32.30	68.0
9	45.5	7.20	1.2	9.8	0.1	3.5				31.8	99.1
	23.19	4.18	0.59	4.37	0.05	1.51				32.11	66.00
10	46.7	6.5	0.8	9.0		4.2		0.6		31.7	99.5
	23.83	3.77	0.40	4.02		1.82		0.10		32.06	66.00
11	45.5	6.8	1.2	9.6		3.3			0.5	31.6	98.5
	23.36	3.97	0.60	4.31		1.44			0.17	32.15	66.00
12	46.5	5.5	0.9	9.0		4.0		1.8	0.5	31.8	100.0
	23.81	3.20	0.45	4.03		1.74		0.32	0.17	32.27	65.99
13	45.4	5.8	1.3	9.9		3.3		3.4		31.9	101.0
	23.20	3.37	0.65	4.43		1.43		0.06		32.31	65.99
14	47.1	3.6	1.4	10.1		3.2		0.2	3.0	31.8	100.4
	24.06	2.09	0.69	4.52		1.39		0.03	1.02	32.20	66.00
15	47.5	3.5	1.4	9.6		3.1		0.3	2.8	32.1	100.3
	24.22	2.03	0.69	4.28		1.34		0.05	0.94	32.43	65.98
16.	45.6	1.0	1.7	9.7	0.6	3.5		9.1		30.2	101.4
	24.39	0.61	0.88	4.54	0.29	1.59		1.68		32.01	65.99
17	44.9	1.3	2.2	9.7	0.4	2.6		9.0	0.5	30.4	101.0
	24.04	0.79	1.14	4.55	0.20	1.18		1.66	0.18	32.26	66.00
18	46.5	2.4	1.6	10.1		2.8	0.1		4.5	31.5	99.5
	24.06	1.41	0.80	4.58		1.23	0.06		1.54	32.31	65.99
19	48.8	1.4	0.1	5.4	0.8	7.4	1.9		2.0	31.9	99.7
	24.94	0.81	0.05	2.42	0.37	3.21	1.21		0.68	32.31	66.00
20	48.9	1.7	0.1	5.1	0.8	7.6	2.2		1.8	32.1	100.3
	24.80	0.98	0.05	2.26	0.37	3.27	1.39		0.60	32.27	65.99
21	50.9	3.2		7.2		4.9	2.9			31.6	100.7
	26.37	1.89		3.26		2.15	1.87			32.44	67.98
22	48.1	5.5		11.0			2.0			34.6	101.2
	22.79	2.96		4.56			1.18			32.50	63.99
23	46.99	8.31	1.17	9.67	0.12	1.09		0.68	0.33	33.61	102.4
	22.37	4.50	0.54	4.03	0.05	0.44		0.11	0.10	31.78	64.00
24	45.81	5.22	2.38	10.9		1.43				32.72	98.50
	22.60	2.93	1.14	4.73		0.60				32.00	64.00
25	45.6	6.61	1.94	9.42	0.12	3.27	0.13	0.05	0.20	32.2	99.5
	23.10	3.81	0.96	4.18	0.06	1.40	0.08	0.01	0.07	32.33	66.00
26	43.8	8.69	1.34	9.19	0.20	2.88	0.12	0.29	0.81	31.7	99.0
	22.36	5.05	0.66	4.11	0.09	1.25	0.88	0.05	0.27	32.08	66.00
27	43.4	8.86	1.30	9.70	0.15	2.99	0.10	0.11	0.16	32.1	98.9
	22.07	5.13	0.64	4.32	0.07	1.29	0.06	0.02	0.05	32.35	66.00
28	45.55	6.35	1.88	8.81	0.63	3.55	Traces	1.28	0.03	31.65	99.73
	23.29	3.69	0.93	3.94	0.29	1.54		0.23	0.01	32.07	65.99
29	44.8	9.11	0.61	10.2	0.22	2.80	0.10	Traces	0.17	32.4	100.4
	22.45	5.19	0.30	4.47	0.10	1.19	0.06		0.06	32.18	66.00
30	46.1	7.15	1.81	9.61	0.25	3.19	0.10	0.01	0.25	31.8	100.3
	23.29	4.11	0.89	4.25	0.11	1.37	0.06		0.08	31.84	66.00
31	46.9	6.65	0.87	9.55	0.13	3.58	0.13	0.16	1.10	32.3	101.4
	23.49	3.79	0.42	4.19	0.06	1.52	0.08	0.03	0.36	32.06	66.00
32	45.7	8.59	1.29	9.57	0.11	3.91	Traces	0.36	0.14	31.92	101.6
	22.85	4.89	0.63	4.19	0.05	1.66		0.06	0.05	31.63	66.01
33	47.1	7.03	1.25	9.46	0.71	3.66	0.16	0.21	0.47	32.1	102.1
	23.45	3.98	0.60	4.12	0.32	1.55	0.10	0.04	0.16	31.68	66.00
34	44.6	9.24	1.36	9.73	0.12	2.93	0.12	0.26	0.45	32.15	100.96
	22.33	5.26	0.66	4.26	0.05	1.24	0.08	0.04	0.15	31.92	65.99
35	49.01	9.78		7.84		4.75				32.2	103.58
	24.72	5.61		3.46		2.03				32.18	68.00
36	40.89	4.41	5.36	10.2		0.38	2.80			32.38	98.45
	20.44	2.51	2.60	4.46		0.16	1.75			32.08	64.00
37	44.07	5.19	5.46	10.2		1.26	2.90			32.66	99.82
	21.76	2.92	2.62	4.42		0.53	1.79			31.96	66.00

Notes: (An. 2) Pb 0.69% (0.11 f.u.), insol. res. 0.75%; (An. 3) Pb 0.96% (0.15 f.u.); (An. 4) insol. res. 2.12%; (An. 5) Pb 0.26% (0.04 f.u.), insol. res. 1.68%; (An. 8) insol. res. 0.88%; (An. 23) Ag 0.11% (0.03 f.u.), Sn 0.16% (0.04 f.u.), Sb 0.14% (0.03 f.u.), Mn 0.03% (0.02 f.u.).
(An. 7) analysis is sample from the Bancairoun deposit (Levy, 1966); (An. 24) analysis is sample from the Radka deposit (Kovalenker *et al.*, 1966); (An. 36 and 37) analyses are samples from the Rajpura-Dariba deposit, India (Mozgova *et al.*, 1992); other analyses are samples from the Tsumeb deposit: (An. 1 and 8) after Francotti *et al.*, 1965; (An. 2) after Pufahl, 1922; (An. 3, 4, and 5) after Viaene *et al.*, 1968; (An. 6) after Levy, 1966; (An. 9—20) after Springer, 1969; (An. 21-22) after Geier *et al.,* 1970; (An. 23) after Spiridonov, 1987; (An. 25-34) after Spiridonov *et al.*, 1992; (An. 35) after Khoroshilova *et al.,* 1988.

Table 4. **Formula based on recalculated germanite analyses**

№	Formula	Valence balance ± Δ	Valence balance %	Me/S
1	$Cu^{+}_{20}(Cu^{2+}_{1.92}Fe^{2+}_{2.09}Zn_{0.61})_{4.62}Fe^{3+}_{2}(Ge^{4+}_{4.13}As^{5+}_{1.07})_{5.2}S_{32}$.	-7.13	11.	0.990
	$Cu^{+}_{16}(Cu^{2+}_{5.92}Zn_{0.61})_{6.53}Fe^{3+}_{4.09}(Ge^{4+}_{4.13}As^{5+}_{1.07})_{5.20}S_{32\cdot17}$	-1.14	1.7	
2	$Cu^{+}_{20}(Cu^{2+}_{3.38}Fe^{2+}_{2.23}Zn_{1.31}Pb^{2+}_{0.11})_{7.03}Fe^{3+}_{2}(Ge^{4+}_{2.79}As^{5+}_{2.20})_{4.99}S_{31\cdot98}$	-1.74	2.7	1.064
3	$Cu^{+}_{20}(Cu^{2+}_{1.57}Fe^{2+}_{2.55}Zn_{1.96}Pb^{2+}_{0.15})_{6.23}Fe^{3+}_{2}(Ge^{4+}_{4.57}Ga^{3+}_{0.86}As^{5+}_{0.60})_{6.03}S_{31\cdot74}$	-1.16	1.8	1.079
4	$Cu^{+}_{20}(Cu^{2+}_{3.98}Fe^{2+}_{0.74}Zn_{1.32})_{6.04}Fe^{3+}_{2}(Ge^{4+}_{4.02}As^{5+}_{1.85})_{5.87}S_{32\cdot09}$	-0.77	1.2	1.057
5	$Cu^{+}_{20}(Cu^{2+}_{0.38}Fe^{2+}_{4.29}Zn_{1.79}Pb^{2+}_{0.04})_{6.5}Fe^{3+}_{2}(Ge^{4+}_{3.18}As^{5+}_{2.13})_{5.31}S_{32\cdot19}$	-2.01	3.1	1.049
6	$Cu^{+}_{20}(Cu^{2+}_{1.91}Fe^{2+}_{1.78}Zn_{0.72})_{4.41}Fe^{3+}_{2}(Ge^{4+}_{4.21}As^{5+}_{1.39})_{5.60}S_{33\cdot99}$	-9.37	14.	
	$Cu^{+}_{16}(Cu^{2+}_{5.91}Zn_{0.72})_{6.04}Fe^{3+}_{3.78}(Ge^{4+}_{4.21}As^{5+}_{1.39})_{5.60}S_{33\cdot99}$	-3.59	5.3	0.941
7	$Cu^{+}_{20}(Cu^{2+}_{3.50}Fe^{2+}_{2.89})_{6.39}Fe^{3+}_{2}(Ge^{4+}_{4.16}As^{5+}_{1.80})_{5.96}S_{31\cdot65}$	+1.12	1.7	1.085
8	$Cu^{+}_{20}(Cu^{2+}_{3.67}Fe^{2+}_{1.95}Zn_{1.64})_{7.26}Fe^{3+}_{2}(Ge^{4+}_{4.28}As^{5+}_{2.16})_{6.44}S_{32\cdot30}$	+3.84	5.6	
	$Cu^{+}_{22}(Cu^{2+}_{1.67}Fe^{2+}_{1.95}Zn_{1.64})_{5.26}Fe^{3+}_{2}(Ge^{4+}_{4.28}As^{5+}_{2.16})_{6.44}S_{32\cdot30}$	+1.84	2.8	1.105
9	$Cu^{+}_{20}(Cu^{2+}_{3.19}Fe^{2+}_{2.18}Zn_{0.59})_{5.96}Fe^{3+}_{2}(Ge^{4+}_{4.37}Ga^{3+}_{0.05}As^{5+}_{1.51})_{5.93}S_{32\cdot11}$	-1.12	1.7	1.055
10	$Cu^{+}_{20}(Cu^{2+}_{3.83}Fe^{2+}_{1.87}Zn_{0.40})_{6.10}(Fe^{3+}_{1.9}W^{4+}_{0.10})_{2}(Ge^{4+}_{4.02}As^{5+}_{1.82})_{5.84}S_{32\cdot06}$	-0.64	1.0	1.059
11	$Cu^{+}_{20}(Cu^{2+}_{3.36}Fe^{2+}_{2.14}Zn_{0.60})_{6.10}(Fe^{3+}_{1.83}Mo^{4+}_{0.17})_{2}(Ge^{4+}_{4.31}As^{5+}_{1.44})_{5.75}S_{32\cdot15}$	-1.66	2.6	1.054
12	$Cu^{+}_{20}(Cu^{2+}_{3.81}Fe^{2+}_{1.69}Zn_{0.45})_{5.95}(Fe^{3+}_{1.51}Mo^{4+}_{0.17}W^{4+}_{0.32})_{2}(Ge^{4+}_{4.03}As^{5+}_{1.74})_{5.77}S_{32\cdot27}$	-1.5	2.3	1.045
13	$Cu^{+}_{20}(Cu^{2+}_{3.20}Fe^{2+}_{1.97}Zn_{0.65})_{5.82}(Fe^{3+}_{1.4}W^{4+}_{0.60})_{2}(Ge^{4+}_{4.43}As^{5+}_{1.43})_{5.86}S_{32\cdot31}$	-1.51	2.3	1.042
14	$Cu^{+}_{20}(Cu^{2+}_{4.06}Fe^{2+}_{1.14}Zn_{0.69})_{5.89}(Fe^{3+}_{0.95}Mo^{4+}_{1.02}W^{4+}_{003})_{2}(Ge^{4+}_{4.52}As^{5+}_{1.39})_{5.91}S_{32\cdot20}$	-1.56	2.4	1.050
15	$Cu^{+}_{20}(Cu^{2+}_{4.22}Fe^{2+}_{1.02}Zn_{0.69})_{5.93}(Fe^{3+}_{1.01}Mo^{4+}_{0.94}W^{4+}_{0.05})_{2}(Ge^{4+}_{4.28}As^{5+}_{1.34})_{5.62}S_{32\cdot43}$	-3.13	4.8	1.036
16	$Cu^{+}_{20}(Cu^{2+}_{4.39}Fe^{2+}_{0.29}Zn_{0.88})_{5.56}(Fe^{3+}_{0.32}W^{4+}_{1.68})_{2}\,(Ge^{4+}_{4.54}Ga^{3+}_{0.29}As^{5+}_{1.59})_{6.42}S_{32\cdot01}$	+1.76	2.7	1.060
17	$Cu^{+}_{20}(Cu^{2+}_{4.04}Fe^{2+}_{0.63}Zn_{1.14})_{5.81}(Fe^{3+}_{0.16}Mo^{4+}_{0.18}W^{4+}_{1.66})_{2}(Ge^{4+}_{4.55}Ga^{3+}_{0.20}As^{5+}_{1.18})_{5.93}S_{32\cdot26}$	-0.54	0.8	1.046
18	$Cu^{+}_{20}(Cu^{2+}_{4.06}Fe^{2+}_{1.01}Zn_{0.80})_{5.87}(Fe^{3+}_{0.40}V^{3+}_{0.06}Mo^{4+}_{1.54})_{2}\,(Ge^{4+}_{4.58}As^{5+}_{1.23})_{5.81}S_{32\cdot31}$	-2.41	3.7	1.043
19	$Cu^{+}_{20}(Cu^{2+}_{4.94}Fe^{2+}_{0.70}Zn_{0.05})_{5.69}(Fe^{3+}_{0.11}V^{3+}_{1.21}Mo^{4+}_{0.68})_{2}(Ge^{4+}_{2.42}Ga^{3+}_{0.37}As^{5+}_{3.21})_{6.00}S_{32\cdot31}$	-0.56	0.9	1.042
20	$Cu^{+}_{20}(Cu^{2+}_{4.80}Fe^{2+}_{0.97}Zn_{0.05})_{5.82}(Fe^{3+}_{0.01}V^{3+}_{1.39}Mo^{4+}_{0.60})_{2}(Ge^{4+}_{2.26}Ga^{3+}_{0.37}As^{5+}_{3.27})_{5.90}S_{32\cdot27}$	-0.4	0.6	1.045
21	$Cu^{+}_{22}(Cu^{2+}_{4.37}Fe^{2+}_{1.76})_{6.13}(Fe^{3+}_{0.13}V^{3+}_{1.87})_{2}(Ge^{4+}_{3.26}As^{5+}_{2.15})_{5.41}S_{32\cdot44}$	-0.83	1.3	1.096
22	$Cu^{+}_{16}(Cu^{2+}_{6.79}Fe^{2+}_{2.14})_{8.93}(Fe^{3+}_{0.82}V^{5+}_{1.18})_{2}Ge^{4+}_{4.56}S_{32\cdot50}$	-6.9	11.	
	$Cu^{+}_{16}Cu^{2+}_{6.79}Fe^{3+}_{2.96}(Ge^{4+}_{4.56}V^{3+}_{1.18})_{5.74}S_{32\cdot50}$	-2.4	3.6	0.969
23	$(Ag^{+}_{0.03}Cu^{+}_{16})_{16.03}(Cu^{2+}_{6.37}Mn^{2+}_{0.02}Zn_{0.54})_{6.93}(Fe^{3+}_{4.50}Mo^{4+}_{0.10}$ $W^{4+}_{0.11}Sb^{3+}_{0.03})_{4.74}(Ge^{4+}_{4.03}Sn^{4+}_{0.04}Ga^{3+}_{0.05}As^{5+}_{0.44})_{4.56}S_{31\cdot78}$	-0.71	1.1	0.904
24	$Cu^{+}_{16}(Cu^{2+}_{6.60}Zn_{0.14})_{7.74}Fe^{3+}_{2.93}(Ge^{4+}_{4.73}As^{5+}_{0.60})_{5.33}S_{32\cdot00}$	-1.81	2.8	1.00
25	$Cu^{+}_{20}(Cu^{2+}_{3.1}Fe^{2+}_{1.97}Zn_{0.96})_{6.03}(Fe^{3+}_{1.84}V^{3+}_{0.08}W^{4+}_{0.01}Mo^{3+}_{0.07})_{2}(Ge^{4+}_{4.18}Ga^{3+}_{0.06}As^{5+}_{1.40})_{5.64}S_{32\cdot33}$	-2.69	4.2	1.040
	$Cu^{+}_{20}(Cu^{2+}_{3.10}Fe^{2+}_{1.81}Zn_{0.96})_{5.87}Fe^{3+}_{2}$ $(Ge^{4+}_{4.18}Ga^{3+}_{0.06}As^{5+}_{1.40}V^{5+}_{0.08}W^{4+}_{0.01}Mo^{3+}_{0.07})_{5.80}S_{32\cdot33}$	-2.376	3.7	
26	$Cu^{+}_{20}(Cu^{2+}_{2.36}Fe^{2+}_{3.45}Zn_{0.66})_{6.47}(Fe^{3+}_{1.6}V^{3+}_{0.08}W^{4+}_{0.05}Mo^{3+}_{0.27})_{2}(Ge^{4+}_{4.11}Ga^{3+}_{0.09}As^{5+}_{1.25})_{5.45}S_{32\cdot08}$	-2.21	3.4	1.057
27	$Cu^{+}_{20}(Cu^{2+}_{2.07}Fe^{2+}_{3.26}Zn_{0.64})_{5.97}(Fe^{3+}_{1.87}V^{3+}_{0.06}W^{4+}_{0.02}$ $Mo^{3+}_{0.05})_{2}(Ge^{4+}_{4.32}Ga^{3+}_{0.07}As^{5+}_{1.29})_{5.68}S_{32\cdot35}$	-2.8	4.3	1.040
	$Cu^{+}_{20}(Cu^{2+}_{2.07}Fe^{2+}_{3.13}Zn_{0.64})_{5.84}Fe^{3+}_{2}(Ge^{4+}_{4.32}Ga^{3+}_{0.07}As^{5+}_{1.29}V^{5+}_{0.06}W^{4+}_{0.02}Mo^{3+}_{0.05})_{5.81}S_{32\cdot35}$	-2.45	3.8	
28	$Cu^{+}_{20}(Cu^{2+}_{3.29}Fe^{2+}_{1.93}Zn_{0.93})_{6.15}(Fe^{3+}_{1.76}W^{4+}_{0.23}Mo^{3+}_{0.01})_{2}(Ge^{4+}_{3.94}Ga^{3+}_{0.29}As^{5+}_{1.54})_{5.77}S_{32\cdot07}$	-1.28	2.0	1.057
29	$Cu^{+}_{20}(Cu^{2+}_{2.45}Fe^{2+}_{3.31}Zn_{0.3})_{6.06}(Fe^{3+}_{1.88}V^{3+}_{0.06}Mo^{3+}_{0.06})_{2}(Ge^{4+}_{4.47}Ga^{3+}_{0.10}As^{5+}_{1.19})_{5.76}S_{32\cdot18}$	-2.11	3.3	1.051
	$Cu^{+}_{20}(Cu^{2+}_{2.45}Fe^{2+}_{3.19}Zn_{0.3})_{5.94}Fe^{3+}_{2}(Ge^{4+}_{4.47}Ga^{3+}_{0.10}As^{5+}_{1.19}V^{5+}_{0.06}Mo^{3+}_{0.06})_{5.88}S_{32\cdot18}$	-1.87	2.9	
30	$Cu^{+}_{20}(Cu^{2+}_{3.29}Fe^{2+}_{2.25}Zn_{0.89})_{6.43}(Fe^{3+}_{1.86}V^{3+}_{0.06}Mo^{3+}_{0.08})_{2}\,(Ge^{4+}_{4.25}Ga^{3+}_{0.11}As^{5+}_{1.37})_{5.73}S_{31\cdot84}$	-0.64	1.0	1.071
31	$Cu^{+}_{20}(Cu^{2+}_{3.49}Fe^{2+}_{2.26}Zn_{0.42})_{6.17}(Fe^{3+}_{1.53}V^{3+}_{0.08}W^{4+}_{0.03}Mo^{3+}_{0.36})_{2}(Ge^{4+}_{4.19}Ga^{3+}_{0.06}As^{5+}_{1.52})_{5.77}S_{32\cdot06}$	-1.21	1.9	1.057
32	$Cu^{+}_{20}(Cu^{2+}_{2.85}Fe^{2+}_{3.00}Zn_{0.63})_{6.48}(Fe^{3+}_{1.89}W^{4+}_{0.06}Mo^{3+}_{0.05})_{2}(Ge^{4+}_{4.19}Ga^{3+}_{0.05}As^{5+}_{1.66})_{5.9}S_{31\cdot63}$	+0.97	1.5	1.085
33	$Cu^{+}_{20}(Cu^{2+}_{3.45}Fe^{2+}_{2.28}Zn_{0.60})_{6.33}(Fe^{3+}_{1.70}V^{3+}_{0.10}W^{4+}_{0.04}Mo^{3+}_{0.16})_{2}(Ge^{4+}_{4.12}Ga^{3+}_{0.32}As^{5+}_{1.55})_{5.99}S_{31\cdot68}$	-0.64	1.0	1.083
34	$Cu^{+}_{20}(Cu^{2+}_{2.33}Fe^{2+}_{3.53}Zn_{0.66})_{6.52}(Fe^{3+}_{1.73}V^{3+}_{0.08}W^{4+}_{0.04}Mo^{3+}_{0.15})_{2}(Ge^{4+}_{4.26}Ga^{3+}_{0.05}As^{5+}_{1.24})_{5.55}S_{31\cdot92}$	-1.37	2.1	1.069
35	$Cu^{+}_{22}(Cu^{2+}_{2.72}Fe^{2}_{3.61})_{6.33}Fe^{3+}_{2}(Ge^{4+}_{3.46}As^{5+}_{2.03})_{5.49}S_{32\cdot18}$	+0.29	0.4	1.113
36	$Cu^{+}_{16}(Cu^{2+}_{4.44}Zn_{2.60})_{7.04}Fe^{3+}_{2.51}(Ge^{4+}_{4.46}As^{5+}_{0.16}V^{5+}_{1.75})_{6.37}S_{32\cdot08}$	+0.84	1.3	0.995
	$Cu^{+}_{16}(Cu^{2+}_{4.44}Zn_{2.60})_{7.04}(Fe^{3+}_{0.25}V^{5+}_{1.73})_{2}(Fe^{3+}_{2.26}Ge^{4+}_{4.46}As^{5+}_{0.16})_{6.88}S_{32\cdot08}$	-2.66	4.1	
37	$Cu^{+}_{20}(Cu^{2+}_{1.76}Fe^{2+}_{2.71}Zn_{2.62})_{7.09}(Fe^{3+}_{0.21}V^{3+}_{1.79})_{2}(Ge^{4+}_{4.42}As^{5+}_{0.53})_{4.95}S_{31.96}$	-3.41	5.3	1.065
	$Cu^{+}_{20}(Cu^{2+}_{1.76}Fe^{2+}_{1.62}Zn_{2.62})_{6.00}(Fe^{3+}_{1.30}V^{3+}_{0.70})_{2}(Ge^{4+}_{4.42}As^{5+}_{0.53}V^{5+}_{1.09})_{6.04}S_{31.96}$	-0.14	0.2	

Notes: All Cu over 16, 20, and 22 atoms in the analyses recalculated based on, respectively, 64, 66, and 68 atoms, is divalent; Sb^{3+}, V^{3+}, Mo^{3+}, and W^{4+} substitute Fe^{3+}; Sn^{4+}, As^{5+}, Ga^{3+}, and V^{5+} substitute Ge^{4+}.

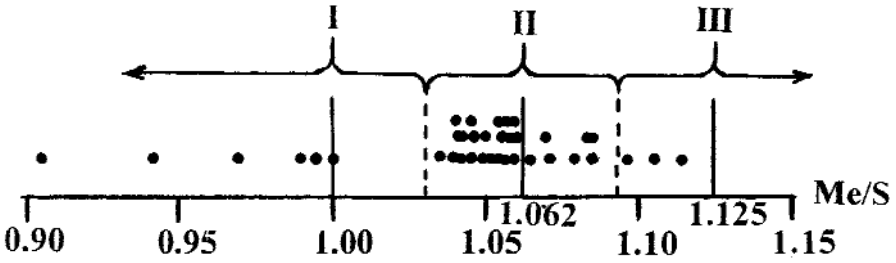

Fig. 3. *Ratio Me/S in analyses of germanite. Groups of the analyses: (I) analyses with the relationship Me/S close to 1; (II) analyses with the relationship Me/S close to 1.062; and (III) analyses with the relationship Me/S close to 1.125.*

This isomorphism was earlier revealed in another complex Ge sulfide, renierite (Bernstein, 1986). In renierite, this dependence is more clearly pronounced than in germanite, possibly due to a more complex character of isomorphism in the latter (because germanite contains admixtures of V, Mo, W, and Ga, which are absent in renierite). According to data of E. Spiridonov (1987), in germanite Fe^{3+} occupies the same site that is occupied by V^{3+} in colusite; therefore, V^{3+} can substitute Fe^{3+} in germanite as well.

A recalculation of the analyses has demonstrated that only 28 analyses from among 37 ones are adequately recalculated to the formula with 66 atoms in the unit cell (in 6 of them, the valence balance slightly exceeds 3%). Six analyses can only be recalculated to the formula with 64 atoms in the unit cell (in 2 of the 6 analyses, the valence balance slightly exceeds 3%), and 3 analyses are well recalculated only on condition that the unit cell contains 68 atoms (Table 4). The Me/S ratio in the analyses varies from 0.904 to 1.113, grouping about the values 1.00, 1.062, and 1.125, corresponding to the Me/S ratios equal to 32:32, 34:32, and 36:32 (Fig. 3). Thus, the cation/anion ratio in real analyses is not constant. This suggests that we deal either with solid solutions or with three different, but similar in the chemical composition and properties, minerals. The second assumption is more probable. Were there an area of solid solutions, the Me/S ratio would be continuous from 1 to 1.125.

So, the 37 analyses are subdivided into three groups calculated based on 64, 66, and 68 atoms in the unit cell. For each group, variations of the principal components (Table 5), their average values (Table 6), as well as the average values of the components occupying different sites in the crystal structure of the mineral (Table 7) are specified. The Cu content generally increases with increasing the number of atoms in the unite cell; the content of Ge and divalent cations decreases in this same direction, which once more illustrates the existing obvious, although relatively slight, differences in the three groups of chemical analyses of germanite, as well as the presence of the isomorphism $Zn^{2+} + Ge^{4+} \rightarrow Cu^{+} + As^{5+}$. Empirical formulae of the average analyses calculated based on different numbers (64, 66, and 68) of atoms in the unit cell will be as follows:

$Cu^{+}_{16}(Cu^{2+}_{6.0}Fe^{2+}_{0.8})_{6.8}Fe^{3+}_{3.5}(Ge^{4+}_{4.4}As^{5+}_{1.1})_{5.5}S_{32.2}$
$\Delta = -1.2$; 1.9%

$Cu^{+}_{20}(Cu^{2+}_{3.3}Fe^{2+}_{2.0}Zn_{0.8})_{6.1}Fe^{3+}_{2.0}(Ge^{4+}_{4.2}As^{5+}_{1.6})_{5.8}S_{32.1}$
$\Delta = -1.2$; 1.9%

$Cu^{+}_{22}(Cu^{2+}_{2.9}Fe^{2+}_{2.4}Zn_{0.6})_{5.9}Fe^{3+}_{2.0}(Ge^{4+}_{4.0}As^{5+}_{2.1})_{5.1}S_{32.2}$
$\Delta = -1.9$; 2.9%

The conclusion on the existence of the three different mineral species can also be derived through drawing an analogy between germanite, on the one hand, and chalcopyrite, talnakhite, mooihoekite, and haycockite, on the other. Until the 1970s, the four last-mentioned minerals were mistaken as a single mineral, chalcopyrite, because of the closeness of their chemical composition and physical properties. In 1967, the work by L. Cabri (1967) was published on cubic chalcopyrite that was found to be an individual mineral species, talnakhite; within 5 years, 2 more mineral species, mooihoekite and haycockite, were discovered (Cabri *et al.*, 1972). Their crystal structures, as well as that of germanite, represent superstructures from the sphalerite structure. As is seen from Table 8, their Me/S ratios are the same as those, around which these ratios are grouped in the real analyses of germanite. This suggests an existence of three independent minerals. Based on the above-presented formulae of chalcopyrite, talnakhite, and mooihoekite, it is easy to obtain germanite formulae with the Me/S ratio equal to 1, 1.062, and 1.125.

In case of substitution $Fe^{3+}_{13} \rightarrow Me^{2+}_{7} + (Ge^{4+}_{5}As^{5+})_{6}$ in chalcopyrite $- Cu^{+}Fe^{3+}S_2 \rightarrow$

Table 5. **Variations in concentrations of the principal components in the chemical composition of germanite, in wt. % (upper row) and in f.u. (lower row)**

An.calc., based on:	Cu from	Cu to	Fe from	Fe to	Zn from	Zn to	Ge from	Ge to	As from	As to	Ge+As+Ga from	Ge+As+Ga to
64 atoms	40.9	48.1	5.2	8.3	0	5.4	9.7	10.9	0	2.6	11.0	13.4
	20.4	22.8	2.9	4.5	0	2.6	4.1	4.7	0	1.07	4.6	6.4
66 atoms	39.4	48.8	1.3	10.7	0	5.5	5.1	10.1	1.3	7.6	11.2	13.8
	20.4	24.9	0.8	6.3	0	2.6	2.3	4.6	0.5	3.27	4.9	6.0
68 atoms	43.6	50.9	3.2	9.8	0	3.10	7.2	9.0	4.7	4.9	12.1	13.7
	23.7	26.4	1.9	5.6	0	1.6	3.3	4.3	2.0	2.2	5.4	6.4

Table 6. **Average concentrations of the principal components in the chemical composition of germanite, in wt. % (upper row) and in f.u. (lower row)**

An.calc., based on:	Cu	Fe	Zn	Fe+Zn	Ge	As	Ge+As+Ga	S
64 atoms	45.2	6.3	1.95	8.2	10.2	1.5	12.6	33.6
	23.3	3.4	0.9	4.3	4.3	0.6	5.4	32.2
66 atoms	45.5	6.0	1.6	7.6	9.1	3.5	13.0	31.7
	23.3	3.5	0.8	4.3	4.1	1.6	5.7	32.1
68 atoms	47.8	6.5	1.0	7.5	8.0	4.8	12.8	31.1
	24.9	3.8	0.5	4.3	3.7	2.1	5.8	32.2

Table 7. **Average concentrations of the principal components in the chemical composition of germanite, in f.u.**

An.calc., based on:	Cu^{+}	Cu^{2+}	Fe^{2+}	Zn^{2+}	ΣMe^{2+}	$Fe^{3+}+V^{3+}+$ Mo+W	Ge^{4+}	As^{5+}	Ge+As+ $Ga+V^{5+}$
64 atoms	16	6.0	0.8	0.0	6.8	3.5	4.4	1.1	5.5
66 atoms	20	3.3	2.0	0.8	6.1	2.0	4.2	1.6	5.8
68 atoms	22	2.9	2.4	0.6	5.9	2.0	4.0	2.1	6.1

Table 8. **Structural characteristics of germanite and minerals of the chalcopyrite group**

Mineral	Formula	Sp. gr	Z	Unit cell parameters, in Å a	c	Reference	Me/S
Chalcopyrite	$Cu^{+}Fe^{3+}S_2 \rightarrow Cu^{+}_{16}Fe^{3+}_{16}S_{32}$	$I\bar{4}2d$	4	5.281	10.401	Hall *et al.*,1973	1
Talnakhite	$Cu^{+}_{9}Fe_8S_{16} \rightarrow Cu^{+}_{18}Fe^{2+}_{2}Fe^{3+}_{14}S_{32}$	$I\bar{4}3m$	16	10.59		Cabri, 1967	1.062
Mooihoekite	$Cu^{+}_{9}Fe_9S_{16} \rightarrow Cu^{+}_{18}Fe^{2+}_{8}Fe^{3+}_{10}S_{32}$	$P\bar{4}2m$	8	10.58	5.37	Cabri *et al.*, 1972	1.125
Germanite	$Cu_{26}Fe_4Ge_4S_{32} \rightarrow Cu^{+}_{16}Cu^{2+}_{10}Fe^{3+}_{4}Ge_4S_{32}$	$P\bar{4}3n$	1	10.58	62(5)	Tettenhorst *et al.*, 1984	1.062

$Cu^{+}_{16}Fe^{3+}_{16}S_{32}$, germanite – $Cu^{+}_{16}Me^{2+}_{7}Fe^{3+}_{3}(Ge^{4+}_{5}As^{5+})_6S_{32}$, with the ratio Me/S = 1 is formed.

In case of substitution $Fe^{3+}_{12} \rightarrow Cu^{+}_{2} + Me^{2+}_{4} + (Ge^{4+}_{4}As^{5+}_{2})_6$ in talnakhite – $Cu^{+}_{9}Fe^{2+}Fe^{3+}_{7}S_{16} \rightarrow Cu^{+}_{18}Fe^{2+}_{2}Fe^{3+}_{14}S_{32}$, germanite $Cu^{+}_{20}Me^{2+}_{6}Fe^{3+}_{2}(Ge^{4+}_{4}As^{5+}_{2})_6S_{32}$ with the ratio Me/S = 1.062 is formed.

In case of substitution $Fe^{2+}_{2}Fe^{3+}_{8} \rightarrow Cu^{+}_{4} + Ge^{4+}_{6}$ in mooihoekite $Cu^{+}_{9}Fe^{2+}_{4}Fe^{3+}_{5}S_{16} \rightarrow Cu^{+}_{18}Fe^{2+}_{8}Fe^{3+}_{10}S_{32}$, germanite $Cu^{+}_{22}Me^{2+}_{6}Fe^{3+}_{2}Ge^{4+}_{6}S_{32}$ with the ratio Me/S = 1.125 is formed. Taking into account the isomorphism $Zn^{2+} + Ge^{4+} \rightarrow Cu^{+} + As^{5+}$, the formula appears as $Cu^{+}_{22}Me^{2+}_{6}Fe^{3+}_{2}(Ge,As)_6S_{32}$, which corresponds to the formula by E. Spiridonov with co-authors (1992). In all the formulae, Me^{2+} is Cu^{2+}, Fe^{2+}, Zn^{2+}.

The similarity between these formulae to those obtained through recalculation of the average analyses for each group is obvious. That once more confirms the logic of the conclusion on the existence of three mineral species chemically close to germanite.

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