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Classification of crystalline substances by crystal systems, crystal classes, Bravais lattices and space groups.

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A totality of 8795 substances of known space group was arranged according to space groups, and within one space group according to chemical categories. Two tables give the realization in absolute numbers and in percentages of the 41 most frequent space groups (≥ 3 %). It was found that the statistics of 1948 (*Crystal Data*, Part I) were already representative; no fundamental changes are to be observed during the subsequent period.

All substances listed in the second edition of Part II of *Crystal Data* (Donnay, Donnay, Cox, Kennard & King, 1963) with a definite space group (and in addition some others) were arranged according to space groups. In the first edition of Part I (Donnay & Nowacki, 1954) 3782 substances were worked through; in the meantime the number increased to 8795. The substances were again divided into chemical categories I to VI [inorganic compounds: I = elements and alloys, including arsenides, borides, hydrides, carbides, nitrides, phosphides and silicides; II = sulphides, sulphosalts, selenides and tellurides; III = oxides and hydroxides; IV = halides, including oxyhalides; V = bromates, chlorates, iodates, carbonates, nitrates, sulphates and tellurates, in which the bonding with oxygen is essentially covalent (Niggli's crystalline compounds of the first kind); VI = aluminates, antimonates, arsenates, borates, cerates, chromates, columbates, ferrites, germanates, manganates, molybdates, osmates, phosphates, platinates, praseodymates, rhenates, silicates, stannates, tantalates, titanates, tungstates, uranates, vanadates and zirconates, in which the bonding with the oxygen is more heteropolar (= Niggli's crystalline compounds of the second kind)] and VII (organic compounds); category VII was again subdivided into 6 (7) divisions [VIIa = inorganic compounds with organic radicals; azides, carbonyls, cyanides, organometallic compounds, siloxanes and silicones; VIIb = aliphatic; VIIc = carbocyclic–alicyclic; VIIc$_2$ = carbocyclic–aromatic; VIId = heterocyclic and VIIe = complex or of unknown constitution]. The following tables were obtained: *A*. Main Table, giving for each space group the substances crystallizing in it (with formula and/or name, reference), arranged according to categories; *B*. Tables of statistical data: (*a*) Distribution of crystalline substances among the 219 space groups (absolute numbers), (*b*) *ditto* (percentages), (*c*) among the 14 Bravais lattices (absolute numbers), (*d*) *ditto* (percentages), (*e*) among the 32 crystal classes (absolute), (*f*) *ditto* (percentages), (*g*) among the 7 crystal systems (absolute), (*h*) *ditto* (percentages), (*i*) among symmorphic, (*), hemisymmorphic (′) and asymmorphic space groups (absolute), (*j*) *ditto* (percentages), (*k*) distribution among the 41 most frequent space groups (absolute) and (*l*) *ditto*, relative (percentages ≥ 3 %).

Tables *B*, (*k*) and (*l*), are given here as Tables 1 and 2. The numbers in parentheses are those of the first edition (Donnay & Nowacki, 1954). The total percentages in Ta-

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* Contribution no. 172.

Table 1. *Distribution of crystalline substances among the*

	I	II	III	IV	V	VI	σ
C_1^1—$P1$*	— —	— —	— —	— —	— —	— —	— —
C_i^1—$P\bar{1}$*	— —	— —	— —	— —	— —	66 (22)	— —
C_2^2—$P2_1$	— —	— —	— —	— —	— —	— —	— —
C_2^3—$C2$*	— —	— —	— —	— —	— —	— —	— —
C_{2h}^2—$P2_1/m$	— —	— —	— —	— —	— —	53 (*6*)	— —
C_{2h}^3—$C2/m$*	— —	— —	— —	34 (*6*)	— —	66 (21)	— —
C_{2h}^5—$P2_1/c$	— —	18 (13)	21 (*6*)	43 (15)	67 (23)	119 (30)	279 (90)
C_{2h}^6—$C2/c'$	— —	*10* (7)	— —	— —	30 (*6*)	76 (36)	153 (*58*)
D_2^3—$P2_12_12$	— —	— —	— —	— —	— —	— —	— —
D_2^4—$P2_12_12_1$	— —	— —	— —	— —	16 (*5*)	— —	— —
D_2^5—$C222_1$	— —	— —	— —	— —	— —	— —	— —
C_{2v}^5—$Pca2_1$	— —	— —	— —	— —	— —	— —	— —
C_{2v}^{17}–$Aba2'$	— —	— —	— —	— —	— —	— —	— —
D_{2h}^{15}–$Pbca$	— —	— —	— —	— —	— —	— —	— —
D_{2h}^{16}–$Pnma$	50 (19)	34 (15)	21 (*3*)	114 (54)	59 (30)	125 (42)	403 (163)
D_{2h}^{17}–$Cmcm$	— —	— —	— —	31 (*6*)	— —	— —	— —
C_4^3—$P4_2$	— —	— —	— —	— —	— —	— —	— —
S_4^2—$I\bar{4}$*	— —	18 (*0*)	— —	— —	— —	— —	— —
C_{4h}^6—$I4_1/a$	— —	— —	— —	— —	— —	46 (38)	— —
D_4^4—$P4_12_12$ D_4^8—$P4_32_12$	— —	— —	— —	— —	— —	— —	— —
D_4^6—$P4_22_12$	— —	— —	— —	— —	— —	— —	— —
D_{2d}^4—$P\bar{4}2_1c$	— —	— —	— —	— —	— —	— —	— —
D_{2d}^{12}–$I\bar{4}2d$	— —	22 (*2*)	— —	— —	— —	— —	— —
D_{4h}^7—$P4/nmm$	— —	— —	— —	44 (15)	— —	— —	— —
D_{4h}^{14}–$P4_2/mnm$	— —	— —	*12* (14)	— —	— —	— —	— —
D_{4h}^{17}–$I4/mmm$*	32 (28)	— —	20 (*6*)	56 (34)	— —	— —	*118* (73)
D_{4h}^{18}–$I4/mcm$	35 (17)	— —	— —	— —	— —	— —	— —
D_{4h}^{19}–$I4_1/amd$	— —	— —	18 (8)	— —	— —	— —	— —
C_3^4—$R3$*	— —	— —	— —	— —	— —	— —	— —
C_{3i}^2—$R\bar{3}$*	— —	— —	— —	65 (28)	— —	*28* (22)	— —
C_{3v}^5—$R3m$*	— —	— —	— —	— —	*13* (9)	— —	— —
D_{3d}^3—$P\bar{3}m1$*	— —	34 (12)	20 (12)	60 (23)	— —	— —	— —
D_{3d}^5—$R\bar{3}m$	*22* (20)	27 (10)	26 (*6*)	72 (25)	— —	47 (26)	208 (90)
D_{3d}^6—$R\bar{3}c'$	— —	— —	*12* (8)	— —	*14* (10)	— —	— —
C_{6h}^2—$P6_3/m$	— —	— —	*9* (8)	— —	— —	*36* (18)	— —
C_{6v}^4—$P6_3mc$	— —	16 (*6*)	— —	— —	— —	— —	— —
D_{6h}^1—$P6/mmm$*	54 (17)	— —	— —	— —	— —	— —	— —
D_{6h}^4—$P6_3/mmc$	149 (119)	34 (20)	23 (14)	— —	— —	— —	237 (162)
T^4—$P2_13$	— —	— —	— —	— —	31 (*6*)	— —	— —
T_h^2—$Pn3'$	— —	— —	— —	— —	20 (*0*)	— —	— —
T_h^3—$Fm3$*	— —	— —	— —	— —	22 (25)	— —	— —
T_h^6—$Pa3$	— —	21 (16)	— —	— —	29 (26)	— —	*97* (66)
T_h^7—$Ia3$	— —	— —	21 (20)	— —	— —	— —	— —
T_d^2—$F\bar{4}3m$*	*21* (18)	25 (14)	— —	*13* (23)	20 (13)	— —	*90* (71)
T_d^6—$I\bar{4}3d$	— —	15 (*0*)	— —	— —	— —	— —	— —
O_h^1—$Pm3m$	94 (80)	— —	— —	34 (19)	— —	77 (20)	220 (130)
O_h^4—$Pn3m$	— —	— —	— —	— —	— —	*4* (16)	— —
O_h^5—$Fm3m$*	147 (88)	85 (43)	50 (21)	197 (123)	*14* (11)	— —	509 (289)
O_h^7—$Fd3m$	101 (41)	32 (8)	89 (58)	— —	— —	66 (21)	297 (136)
O_h^9—$Im3m$*	*23* (25)	— —	— —	— —	— —	— —	— —
O_h^{10}—$Ia3d$	— —	— —	— —	— —	— —	43 (*12*)	— —
Total (only more than 3 %)	662 (472)	381 (158)	309 (163)	750 (359)	294 (147)	765 (312)	2306 (1270)
Total	1130 (659)	566 (239)	557 (258)	1215 (542)	596 (303)	1512 (602)	5576 (2603)

The numbers in italic type

ble 2 are the true ones, *i.e.* they are the totals for more than 3 % (Table 1) expressed as percentages of the totals for all space groups (Table 1, bottom line). The number of the most frequent space groups is 41 (40). Among these the relative number of inorganic compounds (σ) has decreased somewhat, from 49 to 41 %. The realization of the inorganic categories I to VI did not change very much. O_h^5-$Fm3m$ (9/11 %), D_{2h}^{16}-$Pnma$ (7/6 %), O_h^7-$Fd3m$ (5/5 %), C_{2h}^5-$P2_1/c$ (5/4 %), D_{6h}^4-$P6_3/mmc$ (4/6 %), O_h^1-$Pm3m$ (4/5 %), D_{3d}^5-$R\bar{3}m$ (4/4 %) and C_{2h}^6-$C2/c$ (4/0 %) are still the most frequent. For elements and alloys (category I) O_h^5-$Fm3m$ (13/13 %) and D_{6h}^4-$P6_3/mmc$ (13/18 %) predominate, corresponding to the cubic and hexagonal closest packing of spheres. In D_{2h}^{16}-$Pnma$ deformed hexagonal closest packings of spheres are possible (Niggli, 1926), giving the high values for categories IV (9/10 %), V (10/10 %) and VI (8/7 %).

41(40) *most frequent space groups. Absolute numbers*

VII								
a	*b*	c_1	c_2	*d*	c_2+d	*e*	VII	Σ
— —	— —	15 (15)	— —	— —	— —	*2* (1)	— —	— —
41 (*3*)	65 (15)	9 (*3*)	28 (16)	— —	37 (17)	— —	152 (38)	249 (*69*)
— —	76 (31)	84 (64)	35 (14)	42 (2)	77 (16)	20 (3)	266 (118)	284 (127)
— —	— —	20 (19)	— —	*7* (2)	— —	7 (1)	— —	— —
— —	— —	— —	— —	— —	— —	— —	— —	— —
— —	— —	— —	— —	— —	— —	— —	— —	— —
192 (24)	172 (58)	43 (9)	291 (148)	140 (26)	431 (174)	— —	838 (265)	1117 (355)
58 (14)	80 (23)	— —	58 (14)	18 (*1*)	76 (15)	— —	221 (53)	374 (111)
— —	*20* (12)	18 (14)	— —	— —	— —	5 (*0*)	*66* (35)	— —
— —	131 (51)	66 (38)	56 (22)	112 (3)	168 (25)	19 (6)	403 (123)	455 (144)
— —	— —	— —	— —	— —	— —	3 (*0*)	— —	— —
— —	— —	— —	*10* (12)	— —	*11* (13)	— —	— —	— —
— —	— —	— —	*12* (11)	— —	*12* (11)	— —	— —	— —
— —	25 (*4*)	— —	44 (23)	— —	52 (23)	— —	101 (31)	— —
34 (*5*)	28 (20)	— —	— —	— —	— —	— —	*80* (29)	483 (192)
— —	— —	— —	— —	— —	— —	— —	— —	— —
— —	— —	— —	— —	— —	— —	*0* (1)	— —	— —
— —	— —	— —	— —	— —	— —	— —	— —	— —
— —	— —	— —	— —	— —	— —	— —	— —	— —
— —	— —	— —	— —	— —	— —	6 (*0*)	— —	— —
— —	— —	— —	— —	— —	— —	3 (1)	— —	— —
13 (10)	— —	— —	— —	— —	— —	— —	— —	— —
— —	— —	— —	— —	— —	— —	— —	— —	— —
31 (18)	— —	— —	— —	— —	— —	— —	— —	— —
— —	— —	— —	— —	— —	— —	— —	— —	— —
7 (7)	— —	— —	— —	— —	— —	— —	— —	— —
— —	— —	— —	— —	— —	— —	— —	— —	— —
— —	— —	— —	— —	— —	— —	— —	— —	— —
— —	— —	— —	— —	— —	— —	*2* (2)	— —	— —
— —	— —	— —	— —	— —	— —	— —	— —	— —
— —	— —	— —	— —	— —	— —	— —	— —	— —
— —	— —	— —	— —	— —	— —	— —	— —	— —
6 (9)	— —	— —	— —	— —	— —	— —	— —	*218* (103)
— —	— —	— —	— —	— —	— —	— —	— —	— —
10 (9)	— —	— —	— —	— —	— —	— —	— —	— —
— —	— —	— —	— —	— —	— —	— —	— —	— —
— —	— —	— —	— —	— —	— —	— —	— —	— —
— —	— —	— —	— —	— —	— —	— —	— —	242 (163)
— —	— —	— —	— —	— —	— —	— —	— —	— —
— —	— —	— —	— —	— —	— —	— —	— —	— —
— —	— —	— —	— —	— —	— —	— —	— —	— —
8 (6)	— —	— —	— —	— —	— —	— —	— —	— —
— —	— —	— —	— —	— —	— —	— —	— —	— —
— —	— —	— —	— —	— —	— —	— —	— —	— —
— —	— —	— —	— —	— —	— —	— —	— —	— —
— —	— —	— —	— —	— —	— —	— —	— —	223 (130)
— —	— —	— —	— —	— —	— —	— —	— —	— —
32 (23)	— —	— —	— —	— —	— —	— —	— —	547 (313)
— —	— —	— —	— —	— —	— —	— —	— —	303 (141)
— —	— —	— —	— —	— —	— —	— —	— —	— —
— —	— —	— —	— —	— —	— —	— —	— —	— —
388 (120)	577 (210)	255 (159)	512 (260)	312 (33)	841 (294)	63 (15)	1981 (692)	4277 (1779)
814 (254)	853 (326)	303 (175)	750 (361)	418 (48)	1168 (409)	81 (15)	3219 (1179)	8795 (3782)

represent less than 3 %.

Within the 41 most frequent space groups the relative number of organic compounds (VII) increased somewhat from 59 to 62 %. But the relative number of the 41 space groups both for inorganic and organic compounds (Σ) remained constant (47/49 %). The space groups with 2_1 axes and/or glide planes, which yield zigzag chains, are for organic compounds still the most frequent ones [C^5_{2h}-$P2_1/c$ (26/22 %), D^4_2-$P2_12_12_1$ (13/10 %), C^2_2-$P2_1$ (8/9 %) with 26, 13, 8 %, together 50 % (Nowacki, 1951)]. The zigzag chain is the most important 'building unit' (*Baustein*) of the crystalline organic compounds. The triclinic space groups increased a little bit (3–5 %), but not as much as we expected.

The number of space groups which are not realized decreased from 41 to 22, which is to be expected when the total number of compounds is more than doubled (3782

Table 2. *Distribution of crystalline substances among*

Representatives of all other space groups are less than 3 %. * = symmorphic

	I	II	III	IV	V	VI	σ
C_1^1—$P1$*	— —	— —	— —	— —	— —	— —	— —
C_i^1—$P\bar{1}$*	— —	— —	— —	— —	— —	4 (4)	— —
C_2^2—$P2_1$	— —	— —	— —	— —	— —	— —	— —
C_2^3—$C2$*	— —	— —	— —	— —	— —	— —	— —
C_{2h}^2—$P2_1/m$	— —	— —	— —	— —	— —	4 (—)	— —
C_{2h}^3—$C2/m$*	— —	— —	— —	3 (—)	— —	4 (3)	— —
C_{2h}^5—$P2_1/c$	— —	3 (6)	4 (—)	4 (3)	11 (8)	8 (5)	5 (4)
C_{2h}^6—$C2/c'$	— —	— (3)	— —	— —	5 (—)	5 (6)	3 (—)
D_2^3—$P2_12_12$	— —	— —	— —	— —	— —	— —	— —
D_2^4—$P2_12_12_1$	— —	— —	— —	— —	3 (—)	— —	— —
D_2^5—$C222_1$	— —	— —	— —	— —	— —	— —	— —
C_{2v}^5—$Pca2_1$	— —	— —	— —	— —	— —	— —	— —
C_{2v}^{17}–$Aba2'$	— —	— —	— —	— —	— —	— —	— —
D_{2h}^{15}–$Pbca$	— —	— —	— —	— —	— —	— —	— —
D_{2h}^{16}–$Pnma$	4 (3)	6 (7)	4 (—)	9 (10)	10 (10)	8 (7)	7 (6)
D_{2h}^{17}–$Cmcm$	— —	— —	— —	3 (—)	— —	— —	— —
C_4^3—$P4_2$	— —	— —	— —	— —	— —	— —	— —
S_4^2—$I\bar{4}$*	— —	3 (—)	— —	— —	— —	— —	— —
C_{4h}^6—$I4_1/a$	— —	— —	— —	— —	— —	3 (6)	— —
D_4^4—$P4_12_12$ D_4^8—$P4_32_12$	— —	— —	— —	— —	— —	— —	— —
D_4^6—$P4_22_12$	— —	— —	— —	— —	— —	— —	— —
D_{2d}^4—$P\bar{4}2_1c$	— —	— —	— —	— —	— —	— —	— —
D_{2d}^{12}–$I\bar{4}2d$	— —	4 (—)	— —	— —	— —	— —	— —
D_{4h}^7—$P4/nmm$	— —	— —	— —	4 (3)	— —	— —	— —
D_{4h}^{14}–$P4_2/mnm$	— —	— —	— (5)	— —	— —	— —	— —
D_{4h}^{17}–$I4/mmm$*	3 (4)	— —	4 (—)	5 (6)	— —	— —	— (3)
D_{4h}^{18}–$I4/mcm$	3 (3)	— —	— —	— —	— —	— —	— —
D_{4h}^{19}–$I4_1/amd$	— —	— —	3 (3)	— —	— —	— —	— —
C_3^4—$R3$*	— —	— —	— —	— —	— —	— —	— —
C_{3i}^2—$R\bar{3}$*	— —	— —	— —	5 (5)	— —	— (4)	— —
C_{3v}^5—$R3m$*	— —	— —	— —	— —	— (3)	— —	— —
D_{3d}^3—$P\bar{3}m1$*	— —	6 (5)	4 (5)	5 (4)	— —	— —	— —
D_{3d}^5—$R\bar{3}m$*	— (3)	5 (4)	5 (—)	6 (5)	— —	3 (4)	4 (4)
D_{3d}^6—$R\bar{3}c'$	— —	— —	— (3)	— —	— (3)	— —	— —
C_{6h}^2—$C6_3/m$	— —	— —	— (3)	— —	— —	— (3)	— —
C_{6v}^4—$P6_3mc$	— —	3 (—)	— —	— —	— —	— —	— —
D_{6h}^1—$P6/mmm$*	5 (3)	— —	— —	— —	— —	— —	— —
D_{6h}^4—$P6_3/mmc$	13 (18)	6 (8)	4 (5)	— —	— —	— —	4 (6)
T^4—$P2_13$	— —	— —	— —	— —	5 (—)	— —	— —
T_h^2—$Pn3'$	— —	— —	— —	— —	3 (—)	— —	— —
T_h^3—$Fm3$*	— —	— —	— —	— —	4 (8)	— —	— —
T_h^6—$Pa3$	— —	4 (7)	— —	— —	5 (9)	— —	— (3)
T_h^7—$Ia3$	— —	— —	4 (8)	— —	— —	— —	— —
T_d^2—$F\bar{4}3m$*	— (3)	4 (6)	— —	— (4)	3 (4)	— —	— (3)
T_d^6—$I\bar{4}3d$	— —	3 (—)	— —	— —	— —	— —	— —
O_h^1—$Pm3m$*	8 (12)	— —	— —	3 (4)	— —	5 (3)	4 (5)
O_h^4—$Pn3m$	— —	— —	— —	— —	— —	— (3)	— —
O_h^5—$Fm3m$*	13 (13)	15 (18)	9 (8)	16 (23)	— (4)	— —	9 (11)
O_h^7—$Fd3m$	9 (6)	6 (3)	16 (23)	— —	— —	4 (4)	5 (5)
O_h^9—$Im3m$*	— (3)	— —	— —	— —	— —	— —	— —
O_h^{10}—$Ia3d$	— —	— —	— —	— —	— —	3 (—)	— —
Total (only more than 3 %)	59 (72)	67 (66)	55 (63)	62 (66)	49 (49)	51 (52)	41 (49)

to 8795.) It seems that space groups with polar axes (C_{2v}^x, C_{4v}^x, C_{6v}^x) are avoided.

Table 3 gives the absolute number and the percentages for the centric and acentric space groups of each chemical category. The centric space groups are almost everywhere predominant. The centric space groups for the inorganic (σ) and organic substances (VII) are realized by about 80 and 60 %. Only in c_1 and e are acentric ones predominant and d shows 50 %. (In the future the percentages of centric space groups may decrease, according to the analysis of more complex structures).

On the whole it can be said that the statistics of 1948 (Donnay & Nowacki, 1954) were already representative; no fundamental changes are to be observed during the last period.

According to Mackay (1967) the following considerations hold: let M_t be the number of space groups which occur at least t times. If we now plot M_t against t, we obtain a smooth curve, which can be extrapolated to $M_0 \simeq 219$. If we plot $1/M_t$ against t, we obtain a good straight line, which also can be extrapolated to $t=0$, yielding the constant K in the equation $1/M_t = 1/M_0 + t/K$ with the theo-

the 41(40) *most frequent space groups. Percentages*

space groups; ′ = hemisymmorphic; unmarked groups are asymmorphic.

VII								
a	*b*	c_1	c_2	*d*	c_2+d	*e*	VII	Σ
— —	— —	5 (8)	— —	— —	— —	— (7)	— —	— —
5 (—)	8 (5)	3 (—)	4 (4)	— —	3 (4)	— —	5 (3)	3 (—)
— —	9 (9)	28 (36)	5 (4)	10 (4)	7 (4)	25 (20)	8 (9)	3 (3)
— —	— —	7 (11)	— —	— (4)	— —	9 (7)	— —	— —
— —	— —	— —	— —	— —	— —	— —	— —	— —
— —	— —	— —	— —	— —	— —	— —	— —	— —
24 (9)	20 (18)	14 (5)	39 (40)	33 (54)	37 (42)	— —	26 (22)	13 (9)
7 (6)	9 (7)	— —	8 (4)	4 (—)	7 (4)	— —	7 (5)	4 (3)
— —	— (4)	6 (8)	— —	— —	— —	6 (—)	— (3)	— —
— —	15 (15)	22 (21)	7 (6)	27 (6)	14 (6)	23 (40)	13 (10)	5 (4)
— —	— —	— —	— —	— —	— —	4 (—)	— —	— —
— —	— —	— —	— (3)	— —	— (3)	— —	— —	— —
— —	— —	— —	— (3)	— —	— (3)	— —	— —	— —
— —	3 (—)	— —	6 (6)	— —	4 (6)	— —	3 (3)	— —
4 (—)	3 (6)	— —	— —	— —	— —	— —	— (3)	5 (5)
— —	— —	— —	— —	— —	— —	— —	— —	— —
— —	— —	— —	— —	— —	— —	— (7)	— —	— —
— —	— —	— —	— —	— —	— —	— —	— —	— —
— —	— —	— —	— —	— —	— —	— —	— —	— —
— —	— —	— —	— —	— —	— —	7 (—)	— —	— —
— —	— —	— —	— —	— —	— —	4 (7)	— —	— —
— (4)	— —	— —	— —	— —	— —	— —	— —	— —
— —	— —	— —	— —	— —	— —	— —	— —	— —
4 (8)	— —	— —	— —	— —	— —	— —	— —	— —
— —	— —	— —	— —	— —	— —	— —	— —	— —
— (3)	— —	— —	— —	— —	— —	— —	— —	— —
— —	— —	— —	— —	— —	— —	— —	— —	— —
— —	— —	— —	— —	— —	— —	— —	— —	— —
— —	— —	— —	— —	— —	— —	— (13)	— —	— —
— —	— —	— —	— —	— —	— —	— —	— —	— —
— —	— —	— —	— —	— —	— —	— —	— —	— —
— —	— —	— —	— —	— —	— —	— —	— —	— —
— (3)	— —	— —	— —	— —	— —	— —	— —	— (3)
— —	— —	— —	— —	— —	— —	— —	— —	— —
— (3)	— —	— —	— —	— —	— —	— —	— —	— —
— —	— —	— —	— —	— —	— —	— —	— —	— —
— —	— —	— —	— —	— —	— —	— —	— —	— —
— —	— —	— —	— —	— —	— —	— —	— —	3 (4)
— —	— —	— —	— —	— —	— —	— —	— —	— —
— —	— —	— —	— —	— —	— —	— —	— —	— —
— —	— —	— —	— —	— —	— —	— —	— —	— —
— (3)	— —	— —	— —	— —	— —	— —	— —	— —
— —	— —	— —	— —	— —	— —	— —	— —	— —
— —	— —	— —	— —	— —	— —	— —	— —	— —
— —	— —	— —	— —	— —	— —	— —	— —	— —
— —	— —	— —	— —	— —	— —	— —	— —	3 (3)
— —	— —	— —	— —	— —	— —	— —	— —	— —
4 (9)	— —	— —	— —	— —	— —	— —	— —	6 (8)
— —	— —	— —	— —	— —	— —	— —	— —	3 (4)
— —	— —	— —	— —	— —	— —	— —	— —	— —
— —	— —	— —	— —	— —	— —	— —	— —	— —
48 (47)	68 (64)	84 (91)	68 (72)	75 (69)	72 (72)	78 (100)	62 (59)	49 (47)

Table 3. *Distribution of crystalline substances for centric and acentric space groups*

								VII								
	I	II	III	IV	V	VI	σ	*a*	*b*	c_1	c_2	*d*	c_2+d	*e*	VII	Σ
Total numbers																
Centric space groups	954	395	482	1075	440	1230	4576	619	495	83	532	215	747	0	1944	6520
Acentric space groups	176	171	75	140	156	282	1000	195	358	220	218	203	421	81	1275	2275
Percentages																
Centric space groups	84	70	87	88	74	81	82	76	58	27	71	51	64	0	60	74
Acentric space groups	16	30	13	12	26	19	18	24	42	73	29	49	36	100	40	26

retical value $M_0 = 219$. The values $M_{t,\mathrm{obs}}$ and $M_{t,\mathrm{calc}}$ can then be compared, which was done with our new data. The conclusion of Mackay, that there should exist 41 more space groups than have actually been observed, could be confirmed to a certain extent, because the number of space groups without realization decreased from 41 to 22, as mentioned above.

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Rare earth–germanium and –silicon compounds at 5:4 and 5:3 compositions.

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Thirteen new rare earth germanides and eleven new rare earth silicides of 5:4 stoichiometry have been prepared. Lattice constants and structure-types have been determined, principally by single-crystal techniques. For the R_5Ge_4 compounds, all of the lanthanide elements studied show the orthorhombic 5:4 phase previously found for Sm_5Ge_4. (Rare earth metals not studied were Pm, Eu and Yb; in addition to these, Ho and Tm were not studied in the R_5Si_4 series.) The situation for the analogous silicon compounds is more complex. Tb_5Si_4, Dy_5Si_4, Er_5Si_4 and Y_5Si_4 crystallize with the Sm_5Ge_4-type structure; Sm and Gd probably do also, although no single crystals were obtained from these two preparations. La_5Si_4, Ce_5Si_4, Pr_5Si_4 and Nd_5Si_4 form tetragonal crystals, possibly of the Zr_5Si_4 type, whereas Lu_5Si_4 exhibits a monoclinic distortion of the orthorhombic phase. Ce_5Si_3 and Pr_5Si_3 were found to form tetragonal crystals of the Cr_5B_3 structure type. Powder-pattern data in the literature for La_5Si_3 could also be indexed on the basis of this structure type.

The recent characterization (Smith, Johnson & Tharp, 1967) of an orthorhombic phase in the samarium–germanium system as Sm_5Ge_4 has led to the present investigation of other rare earth–germanium and –silicon systems for the occurrence of this new structure type.

Rare earth–silicon compounds at the neighboring composition, R_5Si_3, were shown by Gladyshevskii & Kripyakevich (1964) to be of the $D8_8$ Mn_5Si_3 structure type for R = Gd through Lu. A subsequent investigation (Gladyshevskii, Dvorina, Kulikova & Verkhoglyadova, 1965) of the La–Si system indicated the formation of La_5Si_3, but its structure type was not specified. The present study shows Ce_5Si_3 and Pr_5Si_3 to have a structure of the $D8_l$ Cr_5B_3 type. An examination of the data for La_5Si_3 indicates a similar structure type for this compound.

Experimental

Samples were prepared by mixing appropriate quantities of metal with either germanium or silicon, and arc-melting the mixture in a gettered atmosphere of argon. To improve their homogeneity, the fused buttons were turned over and remelted several times. For the 5:4 germanium compounds all of the rare-earth elements were investigated, with these exceptions: promethium, europium and ytterbium. In addition to these elements, holmium and thulium were not studied in the R_5Si_4 series.

Lattice constants of the various phases were obtained mainly from single-crystal oscillation and Weissenberg photographs. Filtered Cu $K\alpha (= 1{\cdot}5418$ Å) radiation was used. In some instances, front-reflection lines in powder patterns prepared with Cr ($K\alpha = 2{\cdot}2909$ Å) radiation were used to obtain lattice constants. The latter were refined by means of the least-squares program of Heaton, Gvildys & Mueller (1964). Accuracy of the lattice constants derived from single-crystal photographs is estimated to be of the order of 0·5%; those from powder patterns, 0·2 to 0·3%.

Structural results

R_5Ge_4 *compounds*

When germanium is used as the combining element, all of the rare-earth metals studied form the orthorhombic 5:4 phase exhibited by Sm_5Ge_4. This behavior contrasts sharply with the behavior of the rare-earth monogermanides, for

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