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Instructions for use

THE CONNECTION BETWEEN THE PROPERTIES OF ELEMENTS AND COMPOUNDS; MINERALOGICAL-CRYSTALLOCHEMICAL CLASSIFICATION OF ELEMENTS

by

Alexander A. Godovikov* and Yu Hariya

(with 12 text-figures and 3 tables)

Abstract

The described mineralogical-crystallochemical classification bears some similar features with geochemical classification of elements. This similarity emphasizes a greater importance in conforming the vast practical data on petrology. The present classification also bears some resemblance to the technical classification of elements by Berg (1929). The similarity seems logical since the mineralogical-crystallochemical classification of elements unites them on the basis of crystallochemical similarity, determining the type of chemical bonds of the formed compounds, the possibility of crystalline substances. In their turn they determine the common mineral genesis in one mineralogical-crystallochemical group of elements, their co-existence in ores and chemical raw materials and the possiblity of formation of alloys.

Introduction

The Mendeleev Periodic Table serves as a useful basis for understanding the comparative properties of elements. It also provides the foundation for modern research in chemistry, mineralogy, crystallochemistry and many other sciences. The emergence of data on the physical properties of atoms and ions in free conditions, i.e., elements, (including calculations of the last 15—20 years) permits better estimation of the bounds of similarity amongst elements and the principle differences between them. The progression merits further development of a new version of periodic table which will reflect the new data with maximum completencess and allow easy understanding.

Within the new data, particular attention should be focussed upon the theoretical calculations of orbital radii of atoms and ions, their use in the analysis of element properties and the calculation of force characteristics of valence electrons, determining the donor-acceptor properties of elements.

Orbital Radii of Atoms and Ions

In general, it is clear that the nearer the valency electron to the centre of the atom (its nucleus) the more firmly it is bound on the atom. Thus the use of atomic and ionic radii in free conditions, for the estimation of the bonding force between the valency electron and the atomic nucleus, appears most convenient.

However, from the quantum mechanics viewpoint (Born, 1963; Slater, 1960), an electron can exist in any point of the atom's nucleus environment i.e., within an atom

as well as at an essential distance from it. As a result atomic boundaries are both diffuse and indefinite.

At the same time, quantum mechanics permits the calculation of probability of an electron being inside the spheric layer of radius **r.** It also permits the drawing of schematic curves of the radial distribution of electron density, and visualization of the probability of electron surface such as, for example, 95% electron density. The distribution of the electron density, around the nucleus, as the function of the first three quantum numbers (that is, **n, l,** and **m;** the set of electron positions around the nucleus for the electrons with these specified quantum numbers) are termed 'orbitals'. The radii of the main peak of the radial electron density for the individual orbitals of atoms and ions are known as their 'orbital radii'. The radii of the external orbitals of atom or ion define the atomic or ionic radius, and are termed r_{orb} or $r_{orb(n+)}$ respectively.

The analyses of the variations of the orbital atomic radii values (r_{orb}) with the increase of the atomic number (**Z**) allow establishment (Text-fig. 1) of the following recurring regularities of their change (Godovikov, 1977).

1. **The main periodicity** of the change of the orbital atomic radii indicates how elements with maximum orbital radius are present at the beginning of each period of the table, and those with minimum orbital radius at the end of each period (H - He, Li -Ne, Na - Ar, K - Kr etc.,). The main periodicity reflects the decrease in radius with the increase of nuclear charge, brought about in the course of completion of the outermost orbital, and the sudden increases of the radii with the increase of the number of orbits.

2. **The internal periodicity** is characteristically to be found in the steep slope of the line connecting the orbital radii values of **s-elements.** This gradient is lesser for the lines connecting the values of **p-elements,** and there is further decrease for **d** and **f-elements.**

This characteristic is due to the growth of the number of electrons on a subshell undergoing transformation from s-(2) to p-(6), d-(10) or f-elements (14 electrons), while the number of the internal electrons screening the valency electrons from the nucleus remains invariable, and the **d** and **f-elements** are filling their preouter electron subshells.

Internal periodicity permits reference to **s, p, d** and **f-'shrinkage',** i.e., the shrinkage of the orbital radii within the limits of **s, p, d** and **f-elements** of each seperate period. Such shrinkage is most rapid for **s-elements** and least sharp for **f-elements.**

3. **The secondary periodicity** is determined by the difference in the number and type of screening electrons (located between the studied electron and the nucleus) and by the structure of the screening shells. Secondary periodicity expresses a nonlinear change of the atomic orbital radii with the increase of atomic number (**Z**) within a subgroup in the Periodic Table. For example, within Ia-subgroup, one can see a sharp growth in r_{orb} from H to Li. This is due to the occurence of screening $1s^2$ electrons in Li, which are absent in H. The increase in r_{orb} from Li ($1s^2$ screening electrons) up to Na ($1s^2 2s^2 2p^6$ screening electrons) is not so sharp, determining the deviation of the r_{orb} of Na (Text-fig. 1) from the prolongation of the H-Li line to the right.

For the same reason the r_{orb} of K lies not on the prolongation of the Li-Na line, but considerably higher. This is the result of a sharp growth of r_{orb} due to the different

screening system ($1s^2 2s^2 2p^6$ for Na and $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$ for K) and the appearance of a **'d-hole'**.

The r_{orb} values of K, Rb and Cs, having incomplete preouter electron shells (with **d-hole, d-f-hole** and **d-f-g-hole** respectively), lie on an almost straight line. At the same time, the r_{orb} of Fr, the first element after **f-shrinkage**, is a little smaller than the r_{orb} of Cs, the predecessor in the subgroup of the system, and both values are close to each other (2,518 and 2,447 Å for Cs and Fr correspondingly).

Similar reasons are responsible for the nonlinear change of r_{orb} with atomic number (**Z**) in other subgroups of the table, as clearly expressed in Text-fig. 1.

4. **The collateral periodicity** is generated by the difference between the number of electrons on the outer **ns** orbital of **d-elements** and the **(n-1)d orbital** of **f-elements**. For **d-elements** this has resulted in the occurence of two parallel curves rather than a single curve. For the first series of **d-elements**, the curves are Cr-Cu (elements with **4s¹ electrons**) and Sc-Zn (elements with **4s² electrons**). The former lies above latter, in a similar manner to the radii decrease under transition **ns¹ → ns²** for **s-elements**, though the difference between them is lesser. The decrease of the atomic orbital radii for the second **d-element** series, as a result of the transition **5s¹** (curve Nb-Ag) → **5s²** (curve Y-Cd) is further decreased, and for the third **d-element** series the distance between similar curves (Pt-Au with **6s¹** and Zn-Hg with **6s²** electrons) becomes indistinguishable in the plot scale. This reflects the increase of the screening effect due to the increasing number of intermediate electrons under transition, from the first series of **d-elements** (Sc-Zn) to the second (Y-Cd) and then to the third one (Lu-Hg). The **ns¹ → ns²** transitions explain the decrease of atomic orbital radii for the pairs Cr-Mn, Cu-Zn, Ag-Cd and Au-Hg.

The collateral periodicity also defines the two parallel curves for the **f-elements**
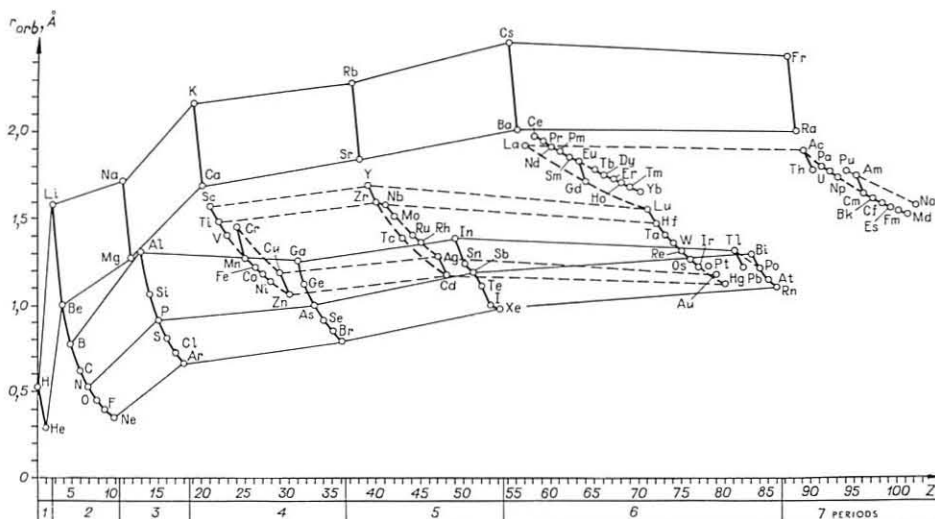
Text-fig. 1 Variation of orbital radii with atomic number (Z). Solid line link the elements of Ia, IIa, IIIa, IVa and Va sub-groups while dotted lines link the elements of IIb and IIIb sub-groups.

(lanthanides) with the same reasoning leading to a decrease in atomic orbital radii for the $6s^2$ electrons.

5. **The double periodicity** relates to the filling of electron orbitals according to Hund's rule. It is difficult to detect these regularities on the r_{orb}-Z plot, but they are clearly visible under analyses of th changes in the values of I_1 or $\eta = 0.529/r_{orb}$ with Z (Godovikov, 1977a). By this method, the dependance of I_1 and η on Z are decribed for elements with p^{1-3}, p^{4-6}, d^{1-5}, d^{6-10}, f^{1-7}, f^{8-14} **electrons** by 'independant' lines. These lines interrupt the lines for **p, d** and **f-elements** on the I_1-Z plot and intersect on the η-Z plot at the points of Va, VIIb and IIIc elements.

Ceno- and Noncenosymmetrical Orbitals and electrons;
The Effect of Inverted Screening

Those orbitals, which are the first in the set of orbitals with constant **n**, i.e., with minimum **l-values** (beginning the lines of each **s, p, d, f orbitals** etc.,) are termed 'cenosymmetrical orbitals'. The electrons in those orbitals are termed the cenosymmetrical electrons (Tshukarev, 1974, 1977). Thus, the **1s ($n = 1$, $l = 0$), 2p ($n = 2$, $l = 1$), 3d ($n = 3$, $l = 2$)** etc., orbitals belong to the cenosymmetrical ones. The important differences between the ceno- and noncenosymmetrical electrons are as follows;
1) only one maximum of an electron density for the cenosymetrical electrons
2) the closer the disposition of th cenosymmetrical electrons to the atom nucleus the stronger their connection with it
3) the radii of cenosymmetrical orbitals for some atoms are smaller than the radii of orbitals having lesser **l-values**.

This last property leads to a peculiar effect termed 'inverted screening', that requires detailed discussion.

Electrons in the atoms, particularly outer ones which take part in chemical bonding (so called valence electrons), are not only under the influence of the forces of attraction from the nucleus but also the complicated forces of the electronic inter action resulting in repulsion. The latter can be expressed, for example, by correlation energy (Tsukarev, 1974).

Such facts lead to a concept of effective nuclear charge **($Z*$)**, which is less than the full nuclear carge (Z) by a value called a screening number σ (screening constant such that $Z* = Z - \sigma$: Slater, 1960; Clementi and Raimondi, 1963; Tshukarev, 1974; Day and Selbin, 1969).

This concept therefore takes into account the weakening of interaction forces between valence electron and the nucleus for preouter electrons of the same electron subshell, shell and orbital. This is known as the 'effect of direct screening'. This theory is good for the atoms having noncenosymmetrical valence electrons, and also for a few atoms having cenosymmetrical electrons in the outer cenosymmetrical orbitals (B, Sc-Cr etc.,).

However, the situation is different for atoms with cenosymmetrical valence electrons, but having the outer orbitals filled with nonsymmetrical electrons, or with their
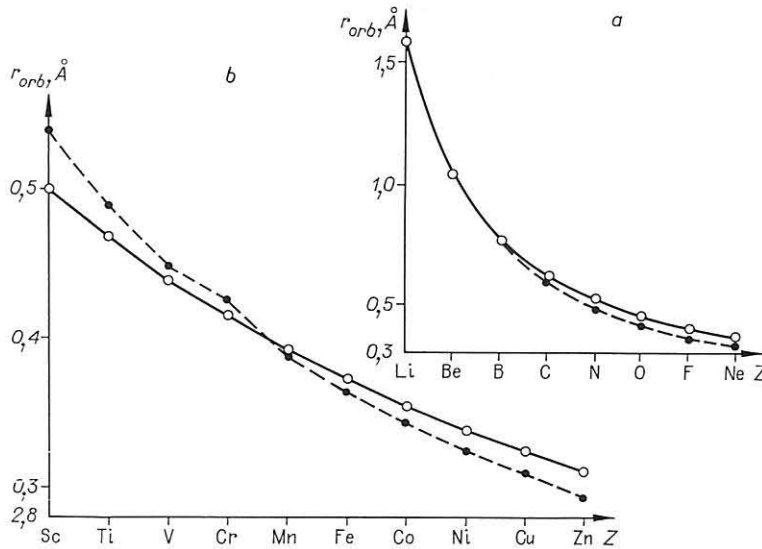
Text-fig. 2 Comparision of orbital radii of Ceno- and Noncenosymmetric elements (dotted and solid lines).
Text fig. 2a shows **2s orbitals** (solid line) and **2p orbitals** (dotted line).
Text fig. 2b shows **3p orbitals** (solid line) and **3d orbitals** (dotted line).

second quantum number **l** being lesser than 1 (Text-fig. 2)

This condition occurs

1) for the majority of **p-elements** of the second period from C to Ne, having a radii of **2p orbitals** which are less than the radii of their **2s orbitals** (Text-fig. 2a),

2) for the atoms of the first **d-element** series with the number of **d electrons** equal or more than 5, having the radii of **3d orbitals** which are less than the radii of **3p orbitals**. This is true for atoms from Mn to Zn (Text-fig. 2b). The same atoms have the r_{orb} of **3s orbitals** a little larger than their **3p orbitals** (Tshukarev, 1977).

This leads to the peculiar conditions, when a part of the valence orbitals (**2p orbitals** of atoms from C to Ne, **3d orbitals** of atoms from Mn to Zn) are screened from the influence of outer forces by the outer, completely filled nonvalence orbitals. This results in 'inverted screening' which causes some interesting results.

As a result of the inverted screening effect, the orbital radii of all **p-elements** of the second group, except B, are determined by the radius of **2s orbitals** rather than **2p orbitals.**

Thus, the elements of the second period lie on the same curve on a r_{orb}-**Z** graph (Text-fig. 2).

The effect of inverted screening explains the low value of electron affinity of F as compared to Cl, the easy oxydation and typicallity of high spin state for elements of the iron family, in comparison to platinoides, and many other specific properties of the elements with cenosymmetrical valence electrons having similar effects. By taking into

account the inverted screening effect it is easy to understand the decrease of the bonding energy in the F molecules, compared with Cl, and other specific properties of molecules and crystalline bodies discussed in earlier papers (Godovikov, 1979).

### Force Characteristics (FC) of the Valence Electrons

The rapid progress of quantum physics and, more especially, the calculation of the electron orbital radii of atoms and ions allows discussion to pass over from the energetic characteristics of the valence electron to the force characteristics. That is, from ionization potential (**I**) and electron affinity of atoms (**F**) having such dimensions as e^2/r to the use of dimensions e^2/r^2 and determining the donor acceptor (acid-basic) properties of elements (Godovikov, 1981). In the above, **e** is electron charge and **r** is the atom, or ion, radius.

The force characteristics (**FC**) can be calculated as the ratio of the electron affinity (for the neutral atom), or ionization potential (for cations), to the orbital radius of the atom or the ion, and is marked as γ_{orb} and $\gamma_{orb(N+)}$, correspondingly.

The importance of γ_{orb} for the characteristics of the donor-acceptor properties of elements becomes clear from the r_{orb}-F relationship (Text-fig. 3), where several fields of elements having similar acidic-basic properties can be seen.

Use of the I_n-$r_{orb(n+)}$ relationship for all the cations of **s** and **p**-elements (Text-fig. 4a) permits a classification into alkalic, basic, amphoteric, weak acidic and strong acidic. Each having its own proper sector on the graph as shown.

A different picture appears for **d-elements** (Text-fig. 4b). Alkalic cations are completely absent, while the group of cations having basic properties becomes essentially larger.
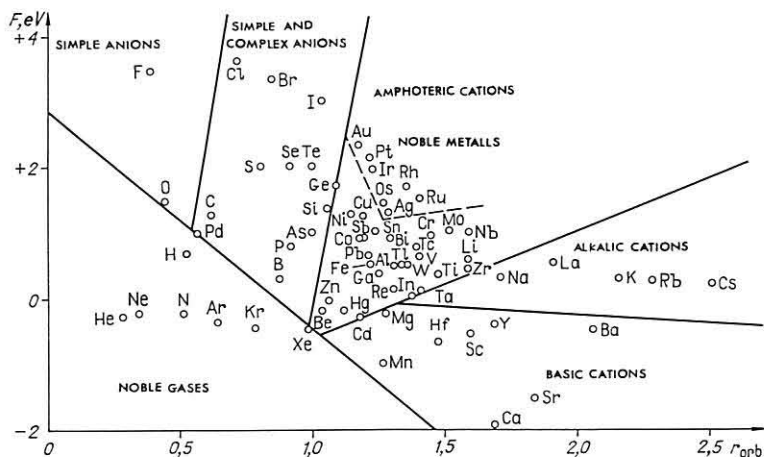

Text-fig. 3 Correlation of electron affinity (**F**) with elemental orbital radii (r_orb).

On the γ_{orb}-Z and $\gamma_{orb(n+)}$-Z graphs (Text-figs. 5, 6) the periodical changes of γ_{orb} and $\gamma_{orb(n+)}$, reflecting all the principle pecularities of the electronic structure for the corresponding cations, can be seen clearly.
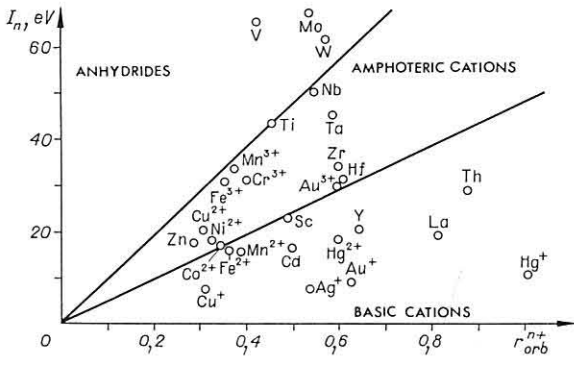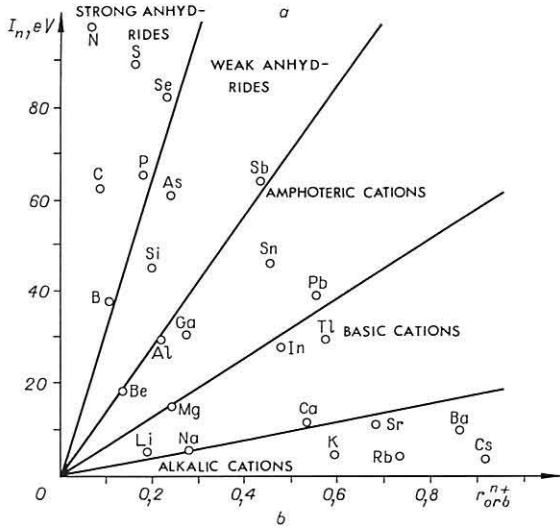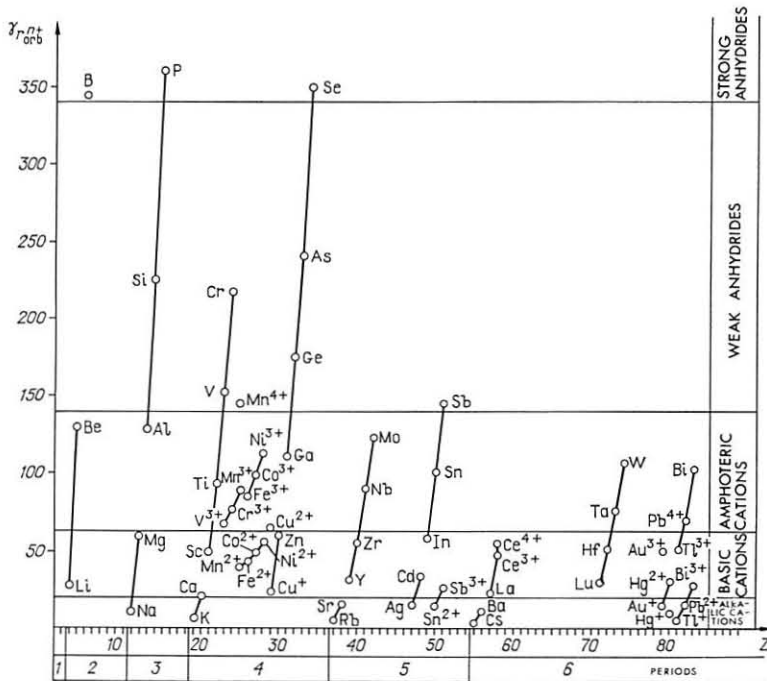

Text-fig. 4 Variation of basic-alkali properties of cations with ionization potential (I_n) and orbital radii of cation (r_{orb}^{n+}).

Text-fig. 4a shows s-and **p-elements**.

Text-fig. 4b shows **d-elements**.
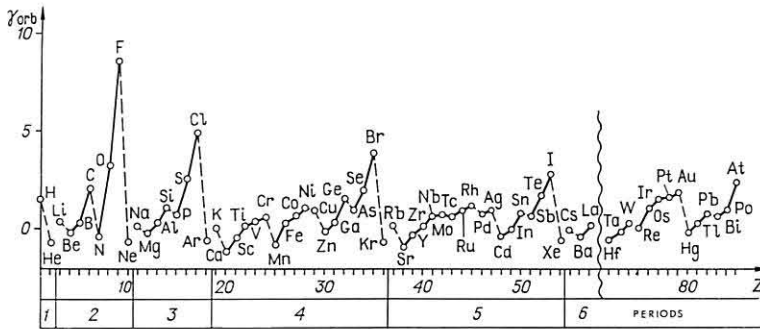
Text-fig. 5 Variation of force characteristics (γ_{orb}^{n+}). with atomic numbewr (**Z**).

Text-fig. 6   Variation of force characteristic (γr_{orb}^{n+}) with atomic number (**Z**).

Analogues: Group, Type, Shell and Shrink

Generalization of the known facts about properties of elements leads to a necessity to distinguish at least four types of similarity among the elements, reflecting the different degrees of analogy between them (Belov et al., 1982; Godovikov, 1981).

1. The elements named as **group analogues,** are the elements belonging to the same group of the Periodic System. Their similarity is limited to the analogy of the number of electrons in the filling electron shell. In some cases, elements have the same group valency; e.g., all the elements of I, III and IV groups. Other groups of the Periodic System do not possess such a similarity. Elements termed as group-analogues have big differences in their properties, which does not typically permit comparison with each other (note the change of the properties for the elements of subgroups of the same group in 1-6).

2. The elements named as **type-analogues** are elements belonging to the same subgroup of the Periodic System. Their similarity expresses not only an analogy of the electrons number on the filling electron shell, but also of the same element type (**s, p, d** or **f**). This is the reason why the analogy between them is more complete than for group analogues, though it can be complicated by various causes (ceno and noncenosymmetrical electrons, prior **d-**and **f-shrinkage** etc.,).

The secondary periodicity phenomenon leads to the broken lines (in some cases

even to loops) of the type-analogues on the graphs of element properties against the increase of atomic number **Z** (Text-fig. 7) (Godovikov, 1977).

3. The elements named as **shell-analogues** are those which belong to the same subgroup and have similar type of shells which are filled by noncenosymmetrical electrons; e.g., K, Rb, Cs and Fr from Ia subgroup, Ag and Au from Ib subgroup, Ca, Sr, Ba and Ra from IIa subgroup, Cd and Hg from IIb subgroup, Ga, In and Tl from IIIa subgroup, Lu and Lr from IIIb subgroup and so on.

In the case of shell-analogues and their compounds, the properties of compounds as a function of **Z** show almost linear relationships (Godovikov, 1978).

4. The elements named as **shrink analogues** include the pairs of elements for which the element with greater **Z** is characterized by **FC** equal or less than that of its precursor in the subgroup (type-analogue), due to **p-, d- or f-shrinkage.**

Shrink-analogues are further subdivided as follows;

a). shrink-analogues beloging to shell-analogues. These are pairs of elements whose **FC** are influenced by prior **f-shrinkage.** They include the following pairs of elements (in cases where the valency is not given the whole-valence cations are meant);
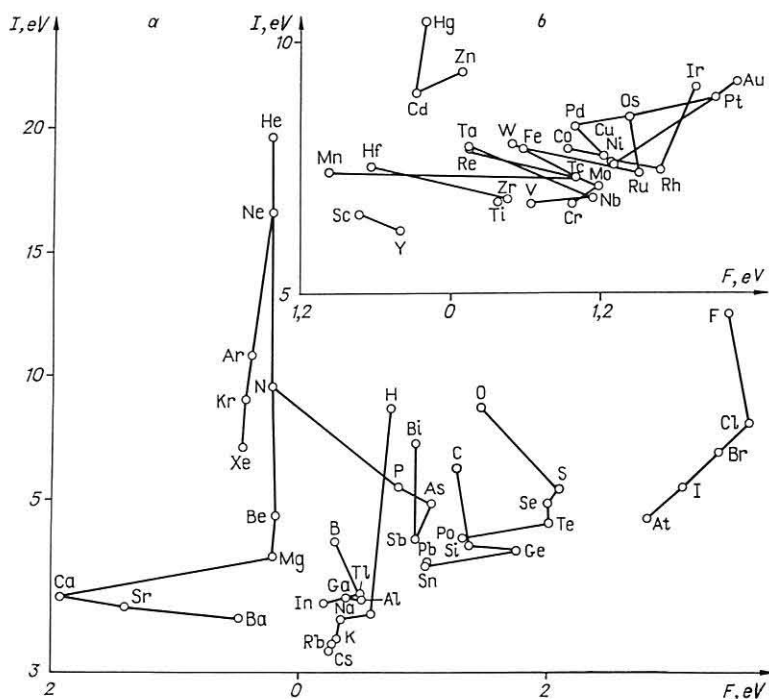
Text-fig. 7 Relationship between 1st ionization potential (**I**) and electron affinity (**F**).
Text-fig. 7a shows *s*- and **p-elements.**
Text-fig. 7b shows **d-elements.**

Pairs of Elements	$\Delta\gamma_{orb\,(n+)}$	Pairs of Elements	$\Delta\gamma_{orb\,(n+)}$
Cs — Fr	0.31	Ru — Os	51.1
Ba — Ra	6.17	Ru^{4+} — Os^{4+}	19.7
Y — Lu	−5.5	Rh^{4+} — Ir^{4+}	22.0
Zr — Hf	6.1	Pd^{4+} — Pt^{4+}	22.0
Nb — Ta	14.5	Ag — Au	−0.5
Mo — W	16.6	Cd — Hg	2.3
Tc — Re	36.6		

The great similarity of properties of the above mentioned elements (especially those with low $\Delta\gamma_{orb}$) can be explained on the basis of their belonging to both shrink and shell-analogues (Achmetov, 1975; Godovikov, 1981).

b). Shrink-analogues belonging to type-analogues. That is, the pairs of elements, whose **FC** are influenced by the prior **d-shrinkage**;

Pairs of Elements	$\Delta\gamma_{orb\,(n+)}$
Al — Ga	17.5
Si — Ge	50.5
P — As	98.6
S — Se	171.4
Cl — Br	320.3

The compounds of these pairs, with strong electron acceptor atoms (F, O) have closely similar properties and, in some cases, form continuous isomorphic series. By contrast, the compounds of elements with lower **FC** (S, Se etc.,) have basically different properties. The former case can be explained by the lesser significance of their own valence electrons, and by their orbital structure, through their high **FC**, while the latter can be reasoned through the stronger influence of the structure of valence orbitals.

c). Shrink-analogues belonging to different types of type-analogue, an example of this being the pair Y — Gd.

Partial **f-shrinkage** before Gd leads, not only to an identical $\Delta\gamma_{orb}^{n+} = 2.0$, but also to the close similarity of the properties of Y and Gd, to which the presence of one **d-electron** in Gd has contributed. The similarities are so strong that the gadolinides, due to common Y impurities are known as 'rare earths' of Yttrium's group [this includes Lu, being not only the shrink, but also the shell-analogue for Y (Taylor and Durby, 1972)].

New Forms of the Periodic Table

Comparing the properties of elements, D.I. Mendeleev stated that there was a difference between many properties of H and the elements of the 2nd period of the system from those of the following elements within the same groups. Taking this into account, in 1870, he named the former elements as 'typical' (Mendeleev, 1958).

From the modern point of view, the 'typical elements' include the cenosymmetrical s-(H, He) and **e-elements** (from B t Ne). Mendeleev also included elements Na and Mg, whose atoms are characterised by cenosymmetrical electrons on the

preouter shell, which becomes the outer one during the formation of full-valence cations. This same structure is repeated in all atoms of the 2nd **p-element** series (from Al to Ar).

These facts explain the appearance of the inflections on the lines of the r_{orb}-**Z** (Text-fig. 1) and I_1-F (Text-fig. 7) graphs, in the points of such elements. Considering all their chemical properties, Mendeleev removed the first s-and **p-elements** from the other elements of the same subgroups (Text-fig. 8). Thus, he already had in view the difference between nonshell-analogues and the close similarity of the shell analogues, although restricting the phenomena to only s-and **p-elements.**

By considering that typical elements are the only elements with cenosymmetrical valence electrons, it is then necessary to add **3d-elements** (Sc-Zn) from amongst **d-elements** and **4f-elements** (lanthanides) from **f-elements.** Thus, typical elements become all cenosymmetrical elements, which differ in their essential properties from the noncenosymmetrical type-analogues (the elements of the subgroups).

This makes it necessary to mark clearly all the typical elements in the Periodic Table. This is possible even without moving the type-analogues from their places by, for example, marking the symbols of such elements with circles and marking the symbols of the elements, forming fullvalence cations with cenosymmetrical outer shells, by dotted circles (Table 1).

It is easy to show on the same table the differences in the properties of elements creating the double periodicity. It is sufficient to print, for example, the symbols of light elements with p^{1-3}, d^{1-5}, f^{1-7} configurations in italics, and those of heavy elements (with p^{4-6}, d^{6-10}, f^{8-14} configurations) as shown (Table 1).

For more detailed discussion of the properties of elements, it is possible to distinguish some small subgroups enclosing the shell-analogues within each subgroup, by the relative displacement of such subgroups. This accounts for the general sequence of elements in the system corresponding to the increase of their **FC** from the left to the right (Table 2).

The new forms of the Periodic Table reflect the following important principles of the Periodic Law of the change of properties of elements;

1. The position of each element on the system is invariable. This is naturally complied by all **s-, p-, d-** and **f-elements.**

2. Each period of the system begins with **s-element** alkali metal (or H in the first period) and ends with an atom of a noble gas, a point reflecting the main periodicity in the change of electron structure of atoms, which depends on the increase of their atoic number. This also corresponds to the increase of **FC** of the elements from the left to the right in each period.

3. Each type of element (**s-, d-, f-** and **p-element**) is marked in its own way. This allows easy visualization of the internal periodicity corresponding to the filling of **s-(to 2), p-(to 6), d-(to 10)** and **f-subshells (to 14 electrons).** This also clearly shows the interrupted periodical character of this relationship defining the relative position of the corresponding elements.

4. Depending on the number of **p-, d-** or **f-elements,** each series of the **p-, d-** and

f-elements is divided into two subfamilies reflecting the double periodicity for each series of such elements (light or p^{1-3}, d^{1-5} and f^{0-6} configurations and heavy or p^{4-6}, d^{6-10} and f^{7-14} configurations). The former is printed in italics and the latter as shown in the Tables.

PERIOD	0	I	II	III	IV	V	VI	VII	VIII
1	—	HYDROGEN H 1.008	—	—	—	—	—	—	
2	HELIUM He 4,0	LITHIUM Li 7,03	BERYLLIUM Be 9,1	BORON B 11,0	CARBON C 12,0	NITROGEN N 14,01	OXYGEN O 16,00	FLUORINE F 19,0	
3	NEON Ne 19,9	SODIUM Na 23,05	MAGNESIUM Mg 24,36	ALUMINIUM Al 27,1	SILICON Si 28,2	PHOSPHORUS P 31,0	SULFUR S 32,06	CHLORINE Cl 35,45	
4	ARGON Ar 38	POTASSIUM K 39,15	CALCIUM Ca 40,1	SCANDIUM Sc 44,1	TITANIUM Ti 48,1	VANADIUM V 51,2	CHROMIUM Cr 52,1	MANGANESE Mn 55,0	IRON Fe 55,9 COBALT Co 59 NICKEL Ni 59 (Cu)
5		COPPER Cu 63,6	ZINC Zn 65,4	GALLIUM Ga 70,0	GERMANIUM Ge 72,5	ARSENIC As 75	SELENIUM Se 79,2	BROMINE Br 79,95	
6	KRYPTON Kr 81,8	RUBIDIUM Rb 85,5	STRONTIUM Sr 87,6	YTTRIUM Y 89,0	ZIRCONIUM Zr 90,6	NIOBIUM Nb 94,0	MOLYBDENUM Mo 96,0	—	RUTHENIUM Ru 101,7 Rh 103,0 PALLADIUM Pd 106,5 (Ag)
7		SILVER Ag 107,93	CADMIUM Cd 112,4	INDIUM Jn 115,0	TIN Sn 119,0	ANTIMONY Sb 120,2	TELLURIUM Te 127	IODINE I 127	
8	XENON Xe 128	CAESIUM Cs 132,9	BARIUM Ba 137,4	LANTHANUM La 138,9 CERIUM Ce 140,2	—	—	—	—	— —
9	—	—	—	—	—	—			
10	—	—	—	YTTERBIUM Yb 173	—	TANTALUM Ta 183	TUNGSTEN W 184	—	OSMIUM Os 191 IRIDIUM Jr 193 PLATINUM Pt 194,8 (Au)
11		GOLD Au 197,2	MERCURY Hg 200,0	THALLIUM Tl 204,1	LEAD Pb 206,9	BISMUTH Bi 208,5	—	—	
12	—	—	RADIUM Rd 225	—	THORIUM Th 232,5	—	URANIUM U 238,5		

MAXIMUM OXIDE TYPE

| R | R^2O | RO | R^2O^3 | RO^2 | R^2O^5 | RO^3 | R^2O^7 | RO^4 |

MAXIMUM HYDRIDE TYPE

| | | | | RH^4 | RH^3 | RH^2 | RH |

D. I. MENDELEEV
1869 — 1905

Text-fig. 8 Periodic system of elements on the basis of group and period.

The transition from light to heavy subfamily corresponds in general to an increase in the value of electron affinity, and an increase in **FC.** As a result, the subfamilies of heavy **p-elements** play, as a rule, the role of anions in different compounds (O^{2-}, F^- and their type-analogues), and after the fulfillment of **p orbitals** the transition to noble gases takes place (VIIIa subgroup).

The transition from light to heavy in the **d-element** series is characterized, through this process, by a transference to elements with a typical non-fullvalence state, and a specific role in the creation of complex compounds and noble gases.

The transition from the light to the heavy subfamily in the **f-element** series corresponds with a decrease in characteristic valency. This is especially visible in the case of curides (for gadolinides, the valency decreases as a result of their belonging to cenosymmetrics), and in the increase in the stability of the complex compounds of these elements.

5. In each type of element **(s, p, d and f)** the elements having outer (valence) cenosymmetrical electrons are marked by circles. Such elements (including Mendeleev's 'typical' elements) differ from other type-analogues in a number of properties, among which it is necessary to point out;

a) much higher **FC** values, attributed to the shift of all the cenosymmetrics to the right, in Table 2, with regard to their type-analogues

b) the generality of the non-fullvalence state, being of prime importance for **3d** and **4f cenosymmetrics.**

6. Among the notable characteristics of elements, which form fullvalence cations and having cenosymmmetrical electrons in their outer shell, is their high **FC** as compared to that of type-analogues with higher **Z** values. The symbols of this type of element are marked with dotted circles.

7. In each subgroup of type-analogues, the small subgroup of shell-analogues are distinguishable, shifted with respect to one another depending on **FC.** Here the symbols of shrink-analogues are printed one under another (e.g., the pairs Al-Ga, Si-Ge, etc.,).

8. The symbols of the elements whose atoms are influenced by prior **f-shrinkage** are marked in this table by rectangles. The **FC** values of the atoms of these elements do not increase with the increase in atomic number **Z** (in the subgroups), but decrease slightly compared to that of the prior elements in the same subgroup (type-analogues).

Finally it is necessary to draw attention to some principle details governing the filling of subshells by electrons, the differences of which lead to the essential differences of the properties of type-analogues. It is worth noting that each new subshell in the first three periods appears only after the completion of the prior subshell with electrons.

The situation is different in the case of the elements of the fourth period. The first of them, K, possesses not $3d^1$, but a $4s^1$ **electron,** the **d-subshell** remains vacant. Thus, it can be said that K has a **d-hole.** The same is true for Ca. The appearance of a **d-hole** for K and Ca leads to the essential changes in properties of these elements, which is more important in determining their properties than expectation based on their variations with the growth of **Z** (see Text-fig. 1-7). This is due to the fact that both K and Ca

begin the series of shell analogues, K-Rb-Cs-Fr and Ca-Sr-Ba-Ra correspondingly.

Considering the facts it seems useful to seperate, amongst **s-elements**, the so-called **s'-elements** i.e., **s-elements** of the first three periods, H, He, Li, Be, Na and Mg, which are typical with **s-electrons** appearing only after complete filling of a preouter shell, and the so-called **s''-elements**, which are those with outer **s-electrons** appearing while the prior subshell remains vacant. To this last subgroup K, Ca (both **3d-hole**), Rb, Sr (**4d** and **4f-holes**), Fr and Ra (**5g, 6d, 6f, 6g** and **6h-holes**) also belong.

The first **3d electron** appears in Sc. For the next **3d-elements**, up to Ni, the numbers of 3d electrons increase. During the transition from Ni to Cu the filling of **3d orbital** takes place, and in the case of Zn the outer **4s orbital** is also filled. Thus Cu and Zn differ essentially from the prior **d-elements** by their completely filled **3d orbitals**. The difference manifests itself in the special position of these elements in the graph of variation of element properties with increase in **Z** (Text fig. 5), as well as in the capacity of Cu to form the extra valence cations (i.e., the cations with the valency exceeding the group valency) due to the participation of **3d-electrons** in the bonding. By contrast Zn possesses only the two valence state, because its **3d-electrons** do not take part in bonding. Similar remarks apply to the last **d-elements** of the second (Ag, Cd) and the third series (Au, Hg). It is necessary to point out that in the second of **d-elements**, Pd, the **d orbital** is completely filled.

All this considered, it is sometimes useful to also divide **d-elements** into **d'-** and **d''-elements**, the former including Sc-Ni and their type-analogues and the latter having Cu, Zn and their type-analogues.

Diagonal Similarity in the Properties of Elements

There is some diagonal similarity between some of the elements. This appears as a result of the increase of **FC** of the elements along the horizontal lines of the Table and their decrease along the verticals. This diagonal similarity is limited by at least two factors;

1) the nonproportional increase of **FC** along the horizontal lines of the Table, leading to an increase in **FC** for the pairs of elements from left to right

2) the difference in the basic properties of **s-, p-, d-** and **f-elements**.

Thus the most complete diagonal similarity exists in the properties of noncenosymmetrical **s-elements**, that is for the pairs Na-Ca, K-Sr, Rb-Ba and Cs-Ra. Availabe (although not complete) data supports this described connection between them.

Thus the crystallochemical similarity of Li-Mg, a typical element pair, is reflected in their isomorphism (although limited) in micas, amphiboles, pyroxenes and garnets. The alloys of the Li-Mg system form two regions of solid solutions, i.e., from Li up to 75% Mg and from Mg up to 17% Li.

The Na-Ca pair exhibits vast isomorphism in complex oxides and some silicates (isomorphism of the type NaSi $\rightleftharpoons$ CaAl in augite, omphacite, plagioclases, zeolites, scapolites etc.,). For the pairs K-Sr, Rb-Ba and Cs-Ra there is insufficient information currently available.

Among the light **d'-elements** it is possible to distinguish the following diagonal pairs; Sc-Zr, Ti-Nb, V-Mo and Cr-Tc. Although some authors consider the isomorphism for the Sc-Zr pair as quite possible it rarely appears in minerals (tortveitite, zircon). However, in artificial complex oxides, which have a coordination number of cations more than 6, the atoms of Zr and Sc are randomly distributed with respect to each other. This remains true even when the ratios of components are integer values (Voronkov et al., 1978).

The Ti-Nb pair is a classical example of heterovalence isomorphism in natural complex oxides and silicates.

In the V-Mo pairing, the replacement has a more limited character in minerals, principally because of the difference in their valence states. The isomorphism between them, of a continuous state, appears only in a metallic state (Makarov, 1973).

There is a lack of information for both the Cr-Tc and Mn-Ru pair. However, for the binary metallic Mn-Ru system vast regions of the solid solutions are known up to 50% Mn from one side, and up to 35% Ru from the other side. From this data, it may be deduced that the similarity between the elements of described pairs decreases with the increase of their atomic number (the increase in **FC**).

Among VIII **p-elements**, especially those under a metallic state, the similarity increases remarkably, a fact proven by the formation of continuous solid solution in the systems Fe-Rh, Co-Pd as well as the solid solutions in the systems Fe-Pd, Fe-Pt, Fe-Ir, Fe-Ru, Co-Pt, Co-Rh, Ru-Os, Ru-Rh, Ru-Ir, Rh-Pd, Rh-Ir.

Two diagonal pairs appear among **d''elements**, namely Cu-Cd and Ag-Hg. In the former case, information was not available, although according to Makarov (1973), isomorphism between them is quite possible. For the Ag-Hg pair it is expressed in the existance of alloys from the Ag side up to 37% Hg.

Among the possible diagonal pairs of **f-elements** only the pair La(Ln)-Th is of some interest. This aids in explaining the isomorphism between the named elements in the complex oxides, thorianite.

The diagonal pairs of **p-elements** are characterized by distinct differences in their **FC**. This explains why the diagonal similarity between them is often absent (i.e., pairs C-P, N-S, O-Cl, Si-As, P-Se, S-Br, Ge-Sb, As-Te and Se-I) or limited. Such is the limited case for B and Si, which play similar crystallochemical roles, for example, under tetrahedric coordination in silicates although without isomorphism. The Ga-Sn pair serves as an example to explain the impurities of Ga ($n.10^{-3}$%) in cassiterite (Makarov, 1973).

Among the elements belonging to different types, diagonally similar pairs, with close similarity, are distinguishable but their number is limited.

Here it is necessary to mention primarily the Ca-Y pair (an **s- and d-element** pairing), showing a wide isomorphism for the compounds with ionic bonds such as complex oxides and fluorides. The pair Zn-In (**d- and p-element** pairing) exhibits continuous isomorphism in chalcogenides (ZnGeAs -InAs, etc.,), due to the unitypical structure of the cations Zn^{2+} and In^{3+} as a result of **sp³-hybridization**.

Data is not available for the pair Cd-Tl (*d* and **p-element** pairing) but, according to

Makarov (1973), isomorphism is quite possible.

The diagonal pair Be-Al (**s-and p-elements**) does not exhibit isomorphism, although Be and Al under tetrahedric coordination play similar crystallochemical roles in complex oxides, berillates, aluminates, berillosilicates, alumosilicates and other similar compounds.

Thus diagonal lines, uniting more than two elements with similar properties do not exist (with the only exception being Na-Ca-Y triades). The reason for this being the distortion of diagonal similarity by shrink analogy.

In this respect, the diagonal becomes modified towards a vertical line as, for example, for the triades of **d-elements**; Sc-Zr-Hf and Ti-Nb-Ta. That is why it is necessary to speak not in terms of diagonal lines but only of 'diagonal pairs'.

Finally it is necessary to point out that besides the described diagonal pairs, which can be termed as straight, inverted diagonal pairs also exist. For a mineralogist the most important of these are S-As, Se-Sb and the Te-Bi pairs. They show a definite similarity in chalcogenides but the reasons for this similarity are not yet quite clear.

The Properties of Atoms and Types of Chemical Bonding in Homodesmical Crystals

Understanding the connection between the atomic properties and chemical bonding type of certain crystals is a fundamental problem in solid state physics and chemistry. Solution of this problem is necessary for the development of general classification procedures of minerals and chemical compounds with certain demanded properties. This involves important queries into the use of scientific progress for the synthesis of compounds and the growth of their crystals. In spite of intensive research in this field the problem remains far from solved.

In the opinion of the author the main reason for the lack of success is an oversimplified approach to the mechanism of chemical bonding. This in turn is related to the general concept of the ionic-covalent character of the bonds, which allow continuous transition from pure covalent to ionic crystals with consequent increase in **FC** of the atoms. The fact that all crystals with metallic bonds are beyond the scope of this present model is clear evidence of deficiency.

Moreover, the bonds for all crystals with covalent, ionic or metallic bonding must be characterized by the degree of covalence ionicity and metallicity. The use of only the degree of ionicity for this purpose leads to many contradictions.

A conclusion on the continuity of the transition from covalent to ionic bond is also not evident, since it must be accompanied by qualitative changes in the character of the chemical bonding from the directional (covalent bond) to the non-directional (ionic bond).

To clarify the depth of these problems, it is convenient to use the well studied compounds with common formula $A^N B^{8-N}$ which include elementaric substances of the IVa subgroup and compounds with covalent, ionic and metallic bonds.

First of all, it is necessary to examine the concept of continuous transition from

covalent to ionic crystals, and vice versa. This must be accompanied by a continuous changing of physical properties of the crystals as a function of the degree of ionicity ie., ΔFC. For that purpose, it is necessary to examine the dependance of melting points and bonding energy on the change of $\Delta\gamma_{orb}$.

In the graph (Text-fig. 9) of the melting temperature against the $\Delta\gamma_{orb}$, the compounds $A^N B^{8-N}$ (where A is s- or p-elements) fall in three separate fields. The change of the melting points, depending on $\Delta\gamma_{orb}$, comes in many different ways. Thus within the $A^{III}B^V$ group, there are apparently great differences in the melting point values, but these quickly decrease with the increase in ΣZ (or average Z) i.e., the degree of metallicity of the bond. Compare the position of compound-analogues, in the curve of transition from the elements of the second period to the elements of the third period
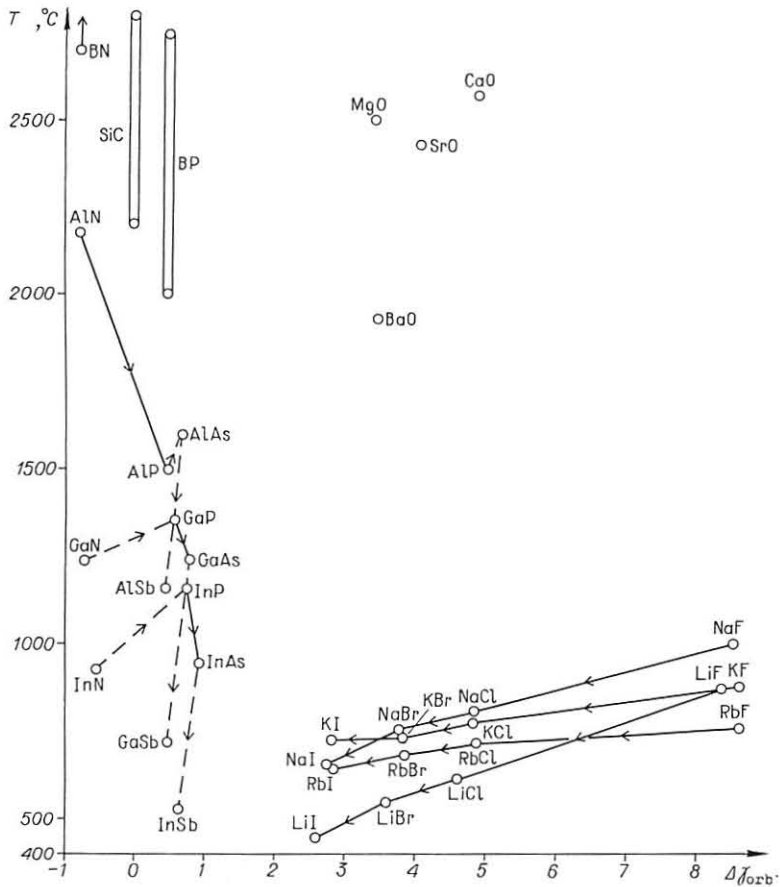
Text-fig. 9 Variation of the melting points of binary compounds $A^N N^{8-N}$ (where A is s- or p-elements) with the diference in force characteristic of the A and B atoms ($\Delta\gamma_{orb}$); lines of "normal" and "anomaly" changine for isocationic compounds as a function of increasing atomic numbers (Z) for B-atoms.

(BN, SiC, BP, AlN) with maximal melting points, to the elements of the fourth and fifth periods (InAs, GaSb, InSb) with minimal melting points. Note also the general decrease of temperatures along the isocationic lines, usually corresponding to the increase of $\Delta\gamma_{orb}$, which takes place with the increase of ΣZ; i.e., the degree of bond metallicity AlN→AlP←AlAs→AlSb, GaN←GaP→GaAs→GaSb or In-N←InP→InAs←InSb with a special position within them for the points of most nitrides.

The decrease of melting temperatures along the lines of the $A^I B^{VII}$ compounds show the opposite tendency. That is, both isocationic lines are directed by the arrows towards each other. Furthermore, the decrease of melting points for them corresponds, not to an increase, but rather a decrease of $\Delta\gamma_{orb}$. This takes place with the growth of ΣZ, i.e., increase of degree of bond metallicity.

This merits special attention, with such great increase of the melting points under transition from the $A^I B^{VII}$ compounds to the $A^{II} B^{VI}$ compounds (impossible to explain as a result solely of change of ΔFC).

It is thus easier to explain this phenomenon by taking into account the fact that the transition from the ionic crystals $A^I B^{VII}$ to the ionic crystals $A^{II} B^{VI}$ is accompanied by a great increase of ion valencies proportional to their changes (from $+1$ and -1 to $+2$ and -2). As a result, the sharp increase of their interactions for ionic crystals is proportional to the product of the ionic charges (Born, 1963). Thus, the **FC** for the ionic crystals, is determined to a greater degree by ion charge, rather than degree of ionicity (i.e., consideration of the isoelectronic compounds of the same period).

The same general picture emerges in the graph (Text-fig. 10) of bond energy (**D₀**) against $\Delta\gamma_{orb}$.
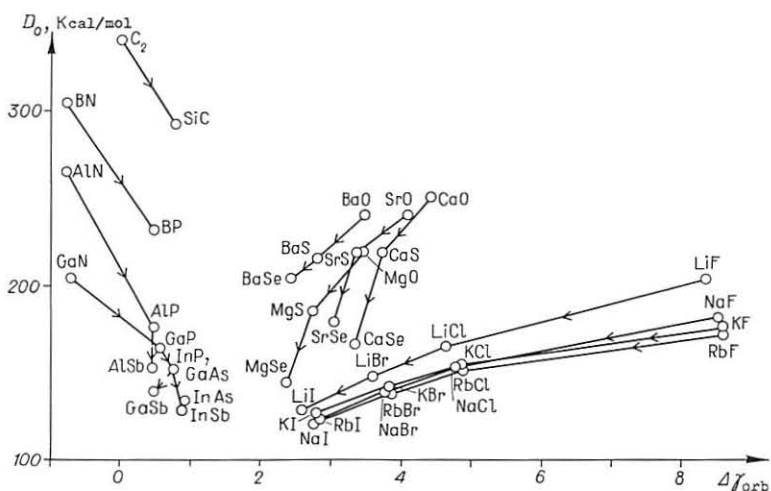
Text-fig. 10 Variation of breaking bond energy (**D₀**) of binary compounds $A^N B^{8-N}$ with force characteristics difference of A and B atoms ($\Delta\gamma_{orb}$).

The aforementioned graphs undoubtedly show the insufficiency of the ionic-covalent bond concept as a full explanation of behaviour. Predicted continuous transition from covalent to ionic crystals is not produced but, instead, a jumplike transitional character is revealed, which is marked by lines of property changes in opposition with the change of $\Delta\gamma_{orb}$, and an absence of the intermediate compounds. From these facts, it also follows that, in any case of the characterization of chemical bond, it is necessary to take into account the degree of metallicity as well as the degree of ionicity.

Mooser and Pearson (1959, 1973 and other publications) were the pioneers in demarcation of the fields of the tetrahedric (covalent) and octahedric (ionic) crystals, $A^N B^{8-N}$, as well as many other crystalline structures. They used the values of electronegativity derived by L. Pauling, as a measure of the ionicity of the bond, and average principle quantum number $\bar{n}$ as a measure of the metallicity of the bond.

Much better results are obtained by using Δ**FC** and particularly $\Delta\gamma_{orb}$ and Σ**Z** instead of $\bar{n}$ as a measure of the metallicity of the bond. Text-fig. 11a shows the graphical
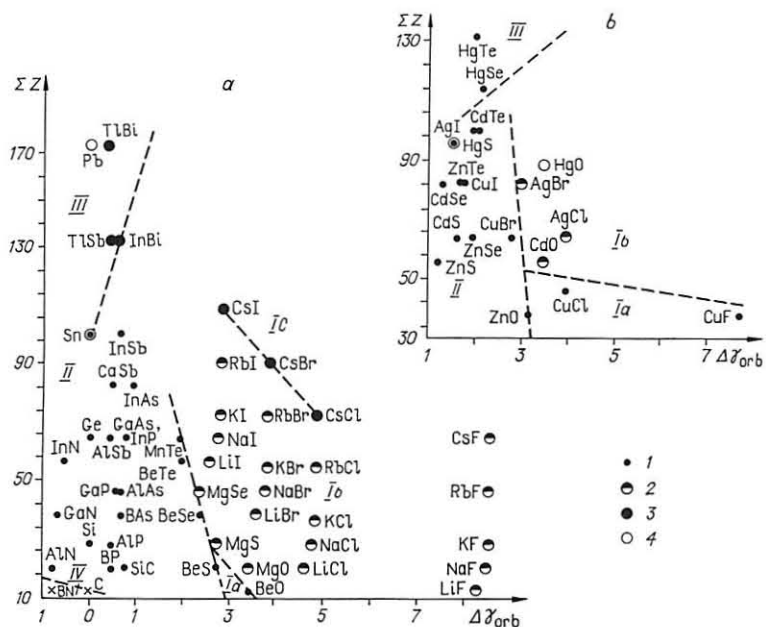
Text-fig. 11 The connection between structure and type of chemical bonding for binary compounds $A^N B^{8-N}$ and their summary atomic number (ΣZ) and force characteristics differences ($\Delta\gamma_{orb}$).

Text-fig. 11a A is s- or p-elements. I is the field of ionic crystals with CN = 4 (Ia), 6 (Ib) and 8 (Ic) correspondingly. II is the field of covalent crystals. III is the field of metallic crystals and IV is the field of molecular crystals. Text-fig. 11b A represents d-elements. I is the field of ionic crystals with CN = 4 (Ia) and 6 (Ib) correspondingly. II is the field of covalent crystals and III is the field of molecular crystals.

In both graphs 1 represents structures with CN = 4, 2 equates to CN = 6, 3 equates to CN = 8 and 4 is for other structures.

relationship between ΣZ and $\Delta\gamma_{orb}$ for 57 $A^N B^{8-N}$ compounds (A = **s-element** and B = **p-elements**) and 6 elementary substances. Observation indicates that the fields for substances having ionic (Ia, Ib, Ic), covalent (II) or metallic (III) and the remaining bonds are clearly distinguishable, having almost straight boundaries between them.

Thus, when speaking about continuous change in the degree of ionicity of covalent bond, in the above mentioned substances, it is necessary to limit the number of substances to the certain relationships of $\Delta\gamma_{orb}$ and ΣZ which mark the boundaries of field II.

On the achievement of a certain critical value of $\Delta\gamma_{orb}$ or ΣZ the substances with covalent bond give way (not continuously but in a jump) to the substances with ionic, metallic or remaining bond. There is a jumplike qualitative change of the character of the chemical bond taking place. After the crossing of certain boundaries the metallic or ionic substances $A^N B^{8-N}$ are formed, instead of covalent (tetrahedrical) substances. Their structures (except that of BeO) have a coordination number (**CN**) more than 4, with molecular crystals being represented by graphite and BN with the graphite structure (field IV).

Generally the same relationships are observed in a similar graph (Text-fig. 11b) for the $A^N B^{8-N}$ compounds with fullvalent cations of **d-elements**. In this case, thirteen points occur in the field of tetrahedric compounds (field II), five points (including HgO) in the field of octahedral crystals with NaCl structure (field Ib), whereas two tetrahedrical compounds, CuCl and CuF, have a position similar to that of BeO in the previous graph (field Ia). The last graph differs from the prior one by a shift of boundaries of the tetrahedric $\rightleftharpoons$ octahedral compounds to higher values of $\Delta\gamma_{orb}$. At the same time, the covalent tetrahedric structure for the compounds $A^N B^{8-N}$, with A being **d-elements**, are more stable. This is proved by sufficiently high stability of the tetrahedric compounds lying near the described boundaries (ZnO, CuBr, CdS and HgS) with hydrolysis, which is not characteristic for the compounds shown on the first graph (BeS, BeSe, BeTe, MgTe), which are easily decomposed even by water vapour.

Similar conclusions, about jumplike transition from the crystals having one type of chemical bond to those of other types, is not only true for $A^N B^{8-N}$ compounds, but also for many others such as $A_2 B_3$, AB_2, $A_2 B$ etc., (Mooser and Pearson, 1959; Pearson, 1973) and oxides of ABO_4 type (Godovikov, 1983).

It is useful to examine some polymorphic pairs when considering the sharp jumplike transition from the crystals of one chemical bond type to those of other types. These illustrate the discussed statements, with a fixed value of temperature and pressure of the phase transition as well as by essential change of the crystal properties i.e., their specific volume. The latter is particularly sensitive to the change of chemical bond from covalent to metallic or ionic, due to the strict orientation of the covalent bondings (because of hybridization of the valence orbitals). This in turn causes the greater specific volume of the covalent crystals in comparison with metallic or ionic ones.

As an example, of the transition from covalent to metallic, one can use the phase transition α-Sn $\rightleftharpoons$ β-Sn taking place under normal pressures and temperatures

(286.35K). Here it is important to remark, that in spite of the fact that transition takes place during an increase in temperature (as a result of which, one can suspect expansion of the substance) it is accompanied by a decrease in specific volume by 25.6%. This results from a change of the type of chemical bond from covalent to metallic one.

The phase transitions α-MnS $\rightleftharpoons \beta$-MnS and α-MnSe $\rightleftharpoons \beta$-MnSe serve as examples of the transition from covalent to ionic srystal. α-MnS and α-MnSe possess tetrahedral structure with covalent bonds (cations Mn_H^{2+}). Both of them are low temperature phases. The high temperature phases β-MnS and β-MnSe, which are stable under room temperature, have the NaCl structure with ionic bond. The corresponding phase transitions are accompanied by decrease of volume (23.5% for MnS and 19.1% for MnSe).

Thus the conditions of formation of the compounds, with a certain type of chemical bond and certain structure (under some fixed limits of physical-chemical parameters with the system) depend on the fundamental properties of the free atoms (elements) forming the compounds i.e., their $\Delta\gamma_{orb}$ and ΣZ. This last statement is very important for the scientific classification of chemical compounds and minerals, because it considers all determination of a compound bonds on the basis of the properties of atoms forming the compounds. Such an approach permits the compound to be referenced to covalent, metallic or ionic crystals, allows understanding of the genesis of the compound structure, makes clear its composition, establishes the boundaries of the isomorphic replacement, clarifies the specificity of its properties and allows establishment of its position among other crystals of the same type and among chemical compounds in general.

All the above conclusions were derived from data on homodesmic crystals, and therefore apply only to compounds of this type. Heterodesmic crystals are subordinated by their own regularities of structure formation and the changes in their properties. This was partially examined in previous work (Godovikov, 1979).

The Mineralogical-Crystallochemical Classification of Elements

Any mineralogical-crystallochemical classification of elements must provide answers to the following queries;
1) which type of compounds certain elements will prefer to form under given conditions of mineral genesis (elementary substance, chalcogenide, oxide, oxysalt, etc.,)
2) whether the element will play a role of a cation or anion of a certain valency
3) which type of chemical bond the resulting mineral compound will have.

For such a classification it is useful to depict, as a basis for the Periodic Table, certain fields uniting elements with similar crystallochemical properties, on the basis of the FC)values $\gamma_i = I_n/r_i$, where I_n = ionization potential and r_i = ionic radius (Text-fig. 12 and Godovikov, 1979). The following 13 fields are recognizable (Table 3):

1. The field of H including only one, but quite unique element, existing in the form H^+ in complex ions (OH^-, H_3O^+, $H_5O_2^+$ etc.,), in the form of H_2O molecules in some oxides with the structure of compounds of inclusions and in hydroxides, many of them oxysalts, which are formed mostly in the earth's crust (under sufficiently high H_2O
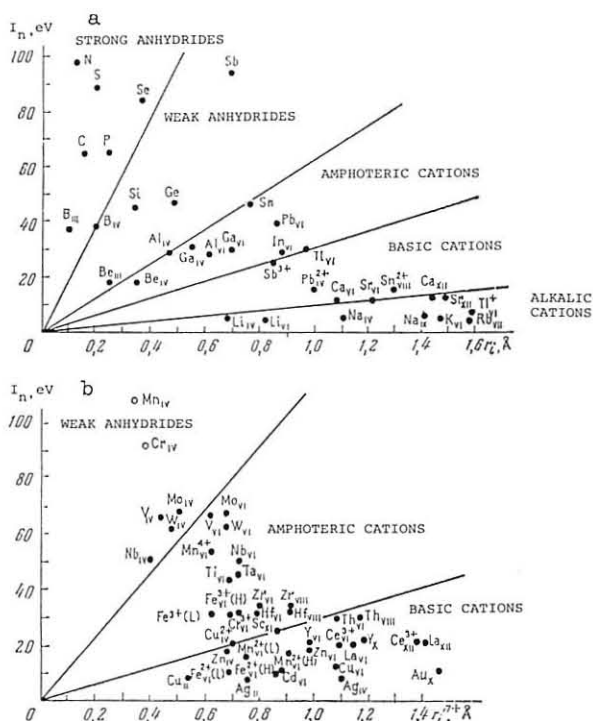
Text-fig. 12 Variation of ionization potential (I_n) with effective ionic radius (r_i) for fullvalence (unmarked) and non-fullvalence (with marked valence).

fugacity). Their role increases from the deep to the upper layers of the earth's crust.

From another viewpoint, hydrogen exists as an anion in hydrides, which are not know between minerals. The specific properties of hydrogen are reflected also in its inherent stability in nature, in gaseous state, and in the upper atmospheric parts, in the atomic state, although gases are not considered as mineralogical objects.

2. The field which contains alkaline and alkaline-earth elements (with low FC) including Li, Mg and their type-analogues with higher Z values. These elements form typical cations, for which the ionic bond with chalcogenes, oxygen and halogenes is characteristic. In addition, their bond with chalcogenes is of very low stability (low degree of covalency), being responsible for the easy hydrolitic decomposition of corresponding chalcogenides. In case of oxocompounds, the γ_i of cations of the described elements is too low in comparison with O^{2-}. This is why these elements from independant monometallic oxysalts with strong oxoanions as a rule while, for example, in silicates, they appear only as partners of cations with higher γ_i (eg., complex silicates, alminosilicates and similar minerals). They are typical for complex oxides. With halogens they form complex, as well as simple (monocationic) halogenides (CaF_2, $NaCl$, KCl, etc.,), which are stable and widespread in nature. At the same time Li, Na and Mg giving cations with much higher γ_i values form binary [$LiAl(Si_2O_6)$, $NaFe(Si_2O_6)$, etc.,] and also monometallic oxysalts [$Mg_2(SiO_4)$, $Li_3(PO_4)$, $Na_2(H_2O)_8(B_4O_5(OH)_4)$, etc.,]. One can explain the pointed specificity of Li, Na and

Mg, in comparison with other elements of this field, by the cenosymmetrical character of their preouter electrons, which become the outer ones in full valence cations. This feature is marked in Table 3 by double horizontal lines separating s'-elements (Li, Na and Mg) from s''-elements (K, Ca and their shell-analogues).

3. The field of rare earth and radioactive elements (TR = Sc, Y and Ln) from one side, and radioactive 5f-elements from the other side (amongst which the independant minerals are known only for Th and U). The rare earth elements are found in minerals mostly as threevalent cations TR^{3+}, for which low FC values affect the ionic bond both with oxygen and also sulfur. Due to much higher valency (cation charge) in respect to cations of alkaline and alkaline-earth elements, i.e., the much higher lattice energy, even the sulfides of rare earth elements are stable to hydrolization. However, they are not known as minerals because of low clarks, and specific features of the geochemistry of the rare earth elements, which form with oxygen, oxides and oxysalts.

Among the latter there are even monometallic oxysalts [eg., monazite $Ce(PO_4)$, xenotime $Y(PO_4)$] and monometallic silicates [such as tortveitite $(ScY)_2(Si_2O_7)$]. The compounds of Ln^{4+} with oxygen, among which only one mineral is known (cerianite CeO_2), are even more stable. Similar FC values to that of Ln^{4+} are possessed by Th^{4+} and U^{4+}, which are known as thorianite ThO_2 and uraninite UO_2. They have the same structure as cerianite. At the same time, the role of U in minerals is more varied because it has known form up to sixvalence ion U^{6+}.

However, the last in oxygenic compounds, which are more widespread among uranic minerals, appears as a big low-charged complex cation of uranil UO_2^{2+}. This resembles some alkalic and alkalic-earth cations in its FC and other properties. This fact explains the appearance of UO_2^{2+} in many secondary phosphates, arsenates, vanadates, molybdates and similar minerals.

The radioactive 5f-elements are isolated from rare earth ones (as noncenosymmetrical) by a double horizontal line.

4. The field of the d'-noncenosymmetrical complexifyers (Zr, Nb) and their shrink-analogues (Hf and Ta). These elements form cations with middle-γ_i which differ in size (high atomic numbers Z). As a result of this, they are typical in complex oxides or silicates where they play a role of weak anion-formators, and in some cases form simple oxides (baddeleite).

Titanium, having diagonal similarity with Nb, adjoins to the previously discussed field from the top. The same is true of V and Cr, showing anion formation properties in some compounds (which increase with the increase of Z).

5. The field of Mo and W. These elements in fullvalence state rarely appear as cations in rare anhydrides, like molybdite, but mostly appear as the components of complex oxides existing on the boundary with oxysalts (the wolframite family → scheelite etc.,) or as weak anion-formators (scheelite). Being in nonfullvalent state, these elements form covalent bonds with chalcogens (molybdenite).

6. The field of d'-cenosymmetrial elements from Ti to Ni (with the exception of Sc and Y which join field 2, due to their low FC alues). These elements in low valence state form cations with low γ_i values, for which the ionic bond with O is typical. From this

point of view such cations are close to Mg^{2+} and Al^{3+}, which also have low γ_i. That is the cause of the isomorphic relationship between these cations (Mg^{2+}, Fe^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+}; Al^{3+}, Fe^{3+}, Mn^{3+}, Cr^{3+} and V^{3+}). For these compounds, the same minerals are typical as for Mg, Al and many binary oxides and oxysalts with Na^+, K^+, Ca^{2+} and other similar cations.

Some of these cations form covalent bonds with chalcogens (S, Se and Te) and are typical in ore minerals. This is true in the case of elements having five and more **d-electrons** (Mn, Fe, Co, Ni) and, as an exception, in the case of Cr^{3+} (dobreelite of meteorites) and V^{4+} (patronite).

The elements of this field containing more than five **d-electrons** i.e., the subfamily of the light **d'elements** of the first series, are known as fullvalent cations. They form simple oxides (rutile, anatase and brookite), complex oxides (ilmenite, perovskite) and complex silicates, containing Ti^{4+}. Nevertheless the γ_i **value** for Ti^{4+} is not sufficient to form a stable anionic complex, causing a similarity between Ti and fullvalence Zr, Nb and their shrink-analogues (which have a separate field in Table 3 as discussed above). At the same time, Ti^{4+}, having co-ordination number (**CN**) $= 5$ and often **CN** $= 4$ in some artificial cases (Ba_2TiO_4, Pb_2TiO_3) exhibits a noticeable transition to oxysalts. On the other hand, V^{5+} and Cr^{6+}, having high γ_i **values,** and for that reason stable oxoanions are typical for vanadates and chromates, which are similar to the fullvalence cations of such elements as Mo and W, and also P and S (especially CrO_4^{2-} and SO_4^{2-} ions).

7. The field of the noble-metallic elements including Ru, Rh, Pd, Ag and their shrink-analogues Os, Ir, Pt and Au, i.e., (the heavy noncenosymmetrical VIIIb and Ib elements). These elements appear frequently in nature as native metals, metallides and intermetallides, often containing the isomorphic impurities of Hg, Pb, Sn, Sb, Bi and Cu. They are known also in covalent chalcogenides (sulfides, selenides, thiosalts and tellurides) and arsenides. The described elements are never established with certainty and may be in the form of natural oxides as well as oxysalts. Only Ag is known in halogenides.

8. The field of the chalcophilic elements with low **FC** (Cu, Zn, Cd, Hg, In, Tl and Pb) and includes the last **d''-elements** as well as Cu and the first heavy **p-elements** for which the covalent bond with chalcogens is typical. Their chalcogenides are most common between minerals, being the main minerals of ore association, and so they can be considered as typical chalcophilics. The oxides of these elements occur rarely and in small amounts (excluding cuprite) as oxydation products of primary chalcogenides. Amongst all these elements which are known in native form, Hg is common enough for different amalgams and native copper is also to be sometimes found in large amounts.

Tl^+ requires some special attention, having big ionic radius and stereochemical inerted E-pair, due to which it is close to K^+ in crystallochemical properties. For this reason Tl often gives isomorphic impurities in some K minerals, in which case Tl^+ appears as a typical cation partner in the ionic bond.

9. The field of chalcophilic elements with middle **FC** which adjoins the previous field from the right. It includes Ge, Sn, As, Sb, Bi, Se and Te from the light **p-elements**

of the same subgroups and are noncenosymmetrical in form (being situated below the double horizontal line of Table 3). These elements are characterized by a dual role, depending on the **FC** values of ligandes. So, in the compounds with chalcogens they appear as typical partners for covalent bond (i.e., they are typical chalcophilic elements). With oxygen, characterized by a high **FC** value, the cations form oxides (anhydrides) having weak → strong acidic properties. They are found in the oxydation zones of ore deposits, usually in small amounts. In this case, the oxysalts are also known in which the described elements play the role anion formators; arsenates, antimonates, selenates, etc.,

10. The field of amphoteric elements consists of two elements, Be and Al, connected by diagonal similarity and known only as fullvalence cations with a middle value of γ_i. Their small dimensions permit them to play a dual role in the compounds with high **FC** partners (O, halogenes), as cations in ionic oxides, oxysalts and halogenides, as weak anion formators in beryllates, beryllosilicates and alumosilicates. The dual role of Al^{3+} appears in the change of **CN** from 6 (as base when $\gamma_i = 46.6$) to 4 (as an anion formator or $\gamma_i = 60.5$), while in both cases Be^{2+} has **CN** = 4 (and $\gamma_i = 52.0$). On the analogy with alumosilicates, some silicates of Be can be called beryllosilicates [phenakite $Be(BeSiO_4)$ etc.,].

Ga also adjoins this field, being a shrink analogue of Al, and is rarely found in the form of its own minerals. The cationic role of Ga manifests itself in the similarity of its properties with [6]Al, leading, together with low clark of Ga, to its endocrypticity in natural oxides, hydroxides and silicates of Al. From another viewpoint, in the compounds with elements characterized by lower **FC** values (chalcogenides with **sp³-hybridization**) Ga appears as a partner on covalent bond (gallates and tiogallates). In this way, its chalcophilic properties are revealed. The same reasoning explains its endocrypticity in sphalerite and some other chalcogenides, with cations having **sp³-hybridization**.

11. The field of light anion formators which includes cenosymmetrial **p-elements** (B, C, N, O, F) but **p-elements** with cenosymmetrical preouter electrons (Si, P, S, Cl and excepting Al) and lies above the double horizontal line. For the elements with high **FC** lying in this field (O, F, Cl) the role of anions is typical in minerals. The other elements typically appear as anion formators of oxysalts, which more commonly exist in nature (nitrites, carbonates, borates, sulfates, phosphates and silicates in decreasing order of γ_i **value**). More rarely, these elements play the role of simple anions (nitrides, carbides, phosphides and silicides which are found mostly in meteorites; S has a special position in sulfides which is widespread in the earth crust).

12. The field of heavy anion formators which includes the noncenosymmetrical (heavy) halogenes Br and I (below the double horizontal line). They appear as anions in rare natural helogenides, mostly with Ag.

13. The special field formed by He, Ne, Ar, Kr, Xe and Rn which exist in nature as noble gases.

Finally it is necessary to mention that within Table 3 the boundaries between 'metallic' (with low to middle **FC**) and 'non-metallic' (with middle to high **FC**) is

Table 1. Periodic table of elements with shifting of elements-analogues. For symbols see explanation of Table 2.

Table 2. Periodical table of elements with little sub-groups (a,b,c,).

ORDINARY TYPE IS USED FOR THE SYMBOLS OF s-ELEMENTS, INCLINED TYPE FOR THE ELEMENTS HAVING p^{1-3}, d^{1-5}, f^{1-7}-ELECTRONS, SOLID TYPE FOR THE ELEMENTS HAVING p^{4-6}, d^{6-10}, f^{7-14}-ELECTRONS.

THE TYPICAL ELEMENTS HAVING CENO-SYMMETRIC OUTER VALENCE ELECTRONS WERE PLACED IN SOLID CIRCLES, THE TYPICAL ELEMENTS HAVING CENO-SYMMETRIC PREOUTER VALENCE ELECTRONS IN DOTTED CIRCLES.

THE SHRINK-ANALOGUES AFTER f-SHRINKAGE WERE PLACED IN SOLID SQUARES (THE PAIRES OF SHELL-ANALOGUES Y-Lu, Zr-Hf etc.), AFTER d-SHRINKAGE IN DOTTED SQUARES (THE PAIRES OF SHELL-ANALOGUES Al-Ga, Si-Ge etc.).

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Table 3. Mineralogical-crystallochemical classification of elements.

THE DOUBLE HORIZONTAL LINES SEPARATE TYPICAL s-, f- AND p-ELEMENTS FROM NONTYPICAL ONES
THE SOLID LINES ARE BOUNDARY BETWEEN METALIC AND NONMETALIC ELEMENTARY SUBSTANCES
ALL LANTHANOIDES ARE PLACED INTO III-C SUBGROUP BECAUSE THEY HAVE MOSTLY 3-VALENCE STATE IN MINERALS

1.HYDROGEN-H
2.ALKALIC AND ALKALI-EARTH ELEMENTS-Li,Na,K,Rb,Cs,Fr;Mg,Ca,Sr,Ba
3.RARE AND RADIOACTIVE ELEMENTS-Sc,Y,Ln,Th,U
4.AMPHOTERIS ELEMENTS-Be,Al,(Ga)
5.CENOSYMMETRIC d'-ELEMENTS-Ti,V,Cr,Mn,Fe,Co,Ni
6.NONCENOSYMMETRIC d'-COMPLEXFORMERS-Zr,Hf,Nb,Ta
7.MOLYBDENIUM AND TUNGSTEN-Mo,W
8.NOBLE METALIC ELEMENTS-Ru,Rh,Pd,Ag;Os,Ir,Pt,Au
9.CHALCOPHYLIC ELEMENTS WITH LOW FC-Cu,Zn,Cd,Hg;(Ga),In,Tl,Pb
10.CHALCOPHYLIC ELEMENTS WITH MIDDLE FC-Ge,Sn;As,Sb,Bi;Se,Te
11.LIGHT ANIONFORMERS-B;C,Si;N,P;O,S;F,Cl
12.HEAVY ANIONFORMERS-Br,I
13.NOBLE GASES-He;Ne,Ar,Kr,Xe,Rn

marked by a thick broken line. This takes into account the diagonal similarity of the pair B-Si and Ge-Sb and the similarity between the shrink-analogues Si-Ge and Sb-Bi.

The described mineralogical-crystallochemical classification bears some similar features with geochemical classification of elements, and especially with that proposed by A.N. Zavaritsky.

This similarity emphasizes a greater importance in conforming with the vast practical data on petrology, as considered by Zavaritsky (1950).

It is interesting to note that the present classification also bears some resemblance to the technical classification of elements by Berg (1929). The similarity seems logical since the mineral-crystallochemical classification of elements unites them on the basis of crystallochemical similarity, determining the type of chemical bonds of the formed compounds, the possibility of crystalline substances. In their turn they determine the common mineral genesis in one mineralogical-crystallochemical group of elements, their co-existence in ores and chemical raw materials and the possibility of formation of alloys. As an example of the latter, one can remember that the common improvers to steel are Co, Ni, Mn, V, Mo and W but not Cu, Zn or Pb. In further contrast, the alloys Cu-Zn, Pb-Sn, Pb-Bi are widely used in industry.

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