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COHESION ENERGY, METALLIC RADIUS AND BONDING ENERGY OF ELECTRONS IN THE IONIC CORE OF METAL ATOMS

ENERGIA KOHEZJI, PROMIENIE METALICZNE A ENERGIA WIĄZAŃ ELEKTRONÓW W RDZENIACH JONOWYCH ATOMÓW METALI

The paper presents the analysis of atomic radii of metals, their cohesion energy (sublimation enthalpy) and the bonding energy of electrons in the highest shell. It has been stated that starting from the alkaline elements, which have the largest radii, the cohesion energy of metals increases linearly with the reciprocal radius, until the d-subshell is half-filled. At a higher number of electrons the cohesion energy linearly decreases (as the inverse metallic radius increases). The dependence has higher slope for the metals situated in more distant groups, compared to the metals from groups 1-5. Similar correlations have been found between the inverse metallic radius and the atomic number (charge of the nucleus) as well as the square root of the bonding energy of electrons in the highest energy level of metal atoms.

A new parameter P_M is proposed to determine the polarizing power of metal atoms in a crystal lattice It is defined as a ratio of square root of the bonding energy of electrons in the outer shell of the ionic core of metal – E_{EBE} and the metallic radius – r:

$$P_M = \frac{\sqrt{E_{EBE}/R}}{r/a_o},$$

where a_o is the radius of the first Bohr orbit of the hydrogen atom and R is the Rydberg's constant. Correlation between the parameter P_M, the metallic radius and the bond energy in metals is discussed. They are referred to melting points of metals and in some properties of the solutions of hydrogen, nitrogen and carbon in metals as well as of the interstitial compounds formed by these non-metals and metals.

Keywords: metallic radius, sublimation entalphy of metals, bonding energy of electrons in the ionic core of metal atoms, polarizing power of metal atoms

W pracy przedstawiono analizę wielkości promieni atomowych metali, ich energii wiązania (entalpii sublimacji) oraz energii wiązania elektronów na ostatniej zapełnionej po-

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784

włoce. Począwszy od pierwiastków alkalicznych, które mają największe promienie, następuje liniowy wzrost energii wiązania od odwrotności promieni metalicznych, aż do zapełnienia w połowie podpowłoki d. Przy dalszym wzroście liczby elektronów w atomie następuje również liniowe, ale obniżanie się energii wiązania, przy czym zależności dla metali leżących w grupach 8-12 są bardziej strome, niż dla metali leżących w grupach 1-5.

Dla określenia zdolności polaryzacyjnej atomów metalu w kryształach zaproponowano nowy parametr P_M wyrażony równaniem:

$$P_M = \frac{\sqrt{E_{EBE}/R}}{r/a_o},$$

gdzie E_{EBE} oznacza energię wiązania elektronów zrębu jonowego, r – promień metaliczny, a_o – promień orbity Bohra atomu wodoru, R – stałą Rydberga. Przeprowadzono dyskusję nad korelacjami pomiędzy parametrem P_M a wielkością promieni metalicznych i energią wiązania w metalach i stopach. W oparciu o powyższe parametry znaleziono przyczyny tak dużych różnic w temperaturach topnienia metali i zróżnicowanych właściwościach roztworów wodoru, azotu, węgla w metalach oraz związków międzywęzłowych utworzonych z tymi pierwiastkami.

1. Introduction

The properties of metals are generally discussed with reference to their position in the periodic table of elements. The discussed parameters involve melting points, cohesion energy, sublimation entalphy, hardness, metallic radius etc. Variations of these parameters are explained by differences in the cohesion energy, connected with the increasing number of valence electrons in atoms and with the changing bond type. These variations are in agreement with theoretical predictions of Engel, Brewer and Pauling [1-3], developed later in [4, 5], which however do not give any explanation for the remarkable differences observed. In crystallochemistry, a particularly useful parameter is metallic radius (half of bond length). Its magnitude is related to the interaction energy of atoms but it appears to be a complex function of the cohesion enthalpy and it depends on the location of elements in the periodic table. Another important parameter, that characterizes atoms in the crystal lattice, is the size of the ionic core (atomic core with the highest energy shell filled) which can be described by means of electron density maps with quite good accuracy. The size of ionic core influences the size of atomic radius. Its interaction with the valence electrons influences also the cohesion energy, which has not been given proper consideration so far.

In this work the above-mentioned parameters are discussed together with the correlations between the metallic radii, cohesion enthalpy and bonding energy of electrons in the ionic core. On the basis of the bonding energy of electrons in the ionic core, a new parameter is proposed, i.e. the polarizing power of metal atom, which can be used to characterize the bonds in solid metals, as well as solutions of hydrogen, nitrogen or carbon in metals or in their interstitial compounds.

2. Cohesion enthalpy and metallic radius

The available melting points of metals are closely related to the energy of metallic bond. Fig. 1 presents the dependence of melting points on the position of elements in the periodic table. The melting points are taken form refs.[6, 7]. In each row, the
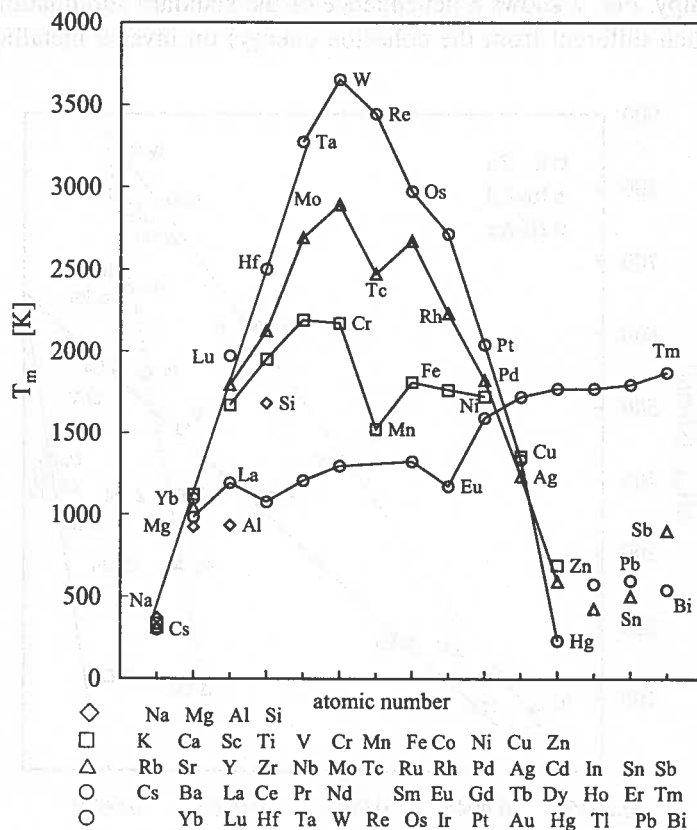

Fig. 1. Melting points of metals (T_m) versus their atomic numbers:
row 3 – points (♦), row 4 (□), row 5 (△), row 6 (o)

melting points increase with an increase of the atomic number and attain maximum for the metals, which have the d-bands, near half-filled. When the number of electrons in the d-band further increases, the melting points gradually decrease. The most regular changes of the melting points are observed in the sixth row, where they form two straight lines. Deviations from the regular behavior are noted for Mn and Tc. These metals and their ions show several abnormal properties, which are related to their electronic structures. The analysis of points representing the 4d and 3d metals of group 8-10 indicates that their behavior deviates from the 5d metals. In the case of rare-earth metals, filling the f- band with electrons only slightly affects the melting points, which finds justification in their electronic structures [8]. Metals with the

d-shells filled (groups 12-15) have relatively low melting points. The melting point dependence shown in Fig. 1 is complex but it is related to the position of metals in the periodic table. Therefore a question arises about the reason for large differences in the melting points of metals.

The metallic radius is characteristic to metal atom and is obviously related to the cohesion enthalpy. Fig. 2 shows a dependence of the standard sublimation enthalpy of metals (not much different from the cohesion energy) on inverse metallic radius. The
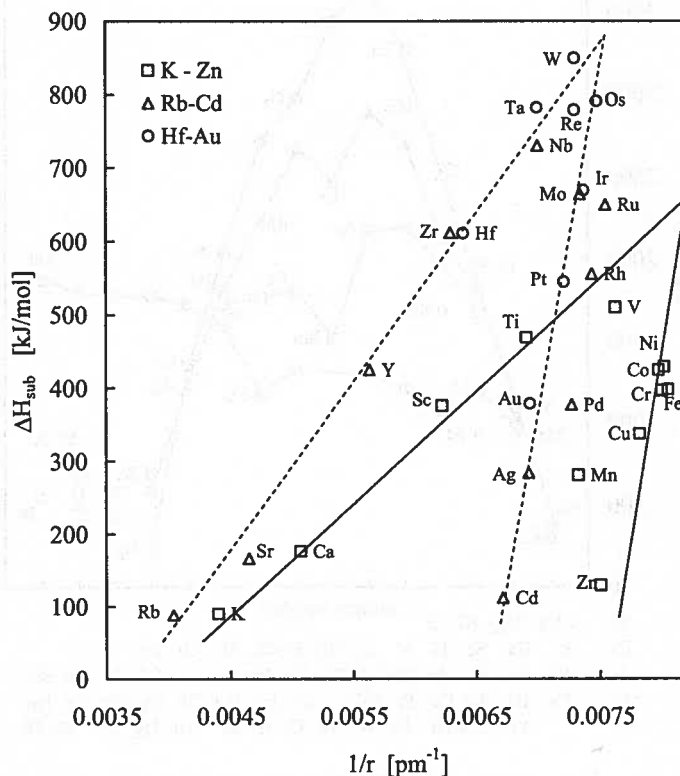

Fig. 2. Correlation between the sublimation energy of metals (ΔH_{sub}) [9, 10] and the inverse metallic radius: row 4 – points ($\square$)., row 5 ($\triangle$), row 6 (o)

values of standard sublimation entalphies were taken from the thermodynamic tables [9, 10], while the metallic radii were calculated from the room-temperature lattice parameters [11, 12]. The points for metals from row 5 and 6 (groups 1-12) are located on two straight lines that intersect, while the metals from row 4 are located on parallel lines. Similarly to Fig. 1, at the higher atomic numbers and the numbers of d electrons, the sublimation entalphy increases linearly with the inverse metallic radius. When the d band is half-filled, for the 4d and 5d metals, the cohesion energy strongly decreases while the metallic radius increases only slightly. For the 3 d metals, when the cohesion

energy change, the metallic radii remain practically constant, with one exception for manganese.

The relations obtained confirm the fact that the metallic radii influence the space distribution of atoms and energy of bonds in metals. Almost linear dependences have been found between the cohesion energies and inverse metallic radii. When the number of d electrons is < 5, the cohesion energy increases linearly with 1/r. When the number of d electrons further increases the atomic radius decreases slightly, while the cohesion energy decreases drastically. The classification of metals in two groups (left and right branch of the plots) confirms the fact that the metals differ in many physical properties. The different types of dependences between the cohesion energy and inverse metallic radius indicate that the radius is dependent not only on the cohesion energy but also on other parameters.

3. Bonding energy of electrons in the ionic core of metals

The bonding energy of electrons in the highest, completely filled, energy shell is a characteristic parameter for the ionic cores of metal atoms. Fig. 3 shows a relation between the square root of the bond energy E_{EBE} of an electron in the highest, filled, electron shell in a crystal divided by the Rydberg's constant, and the charge of the nucleus (atomic number). The data from a number of papers [13-15] were collected and verified by W i l l i a m s [16]. As can be seen in Fig. 3 many points are located along the straight lines, some deviations occur in the case of metals with high atomic numbers in each row. For comparison, the ionization energies E_{IE} of the isolated ions (expressed in the same units) [17, 18] are also given; valence shells are the same as for the above- discussed ionic cores in the crystal lattices of metals. The bonding energy of electrons in the highest filled shell, in the crystal lattice of metal, is much lower than in the case of free ions. This indicates that electrons in these shells are less strongly bonded and therefore the radii of the ionic cores of metals should be larger than the radii of the isolated ions. The lower is the energy of electrons the larger is the radius of the electron shell. Significant differences in the electron energy are observed in the case when the p subshells are filled. In the case of lanthanides (Fig. 3b), the higher number of electrons in the 4f subshell causes a very small increase in the energy of 5p electrons, and similarly the ionization energy of lanthanide ions 3+ (the fourth ionization potential) changes then only slightly [17, 18].

As the energy of electrons in the ionic cores is lower than in the shells of the isolated ions, the ionic cores appear more 'elastic' and can be deformed as a result of atomic interactions (e.g. when doped by foreign atoms). This can occur due to significant differences in the radii of metal ions and ionic cores. This observation is supported by the fact that metals can form solid solutions in a wide concentration range which is not observed for the ionic crystals (chlorides, oxides) in which ions of the same metals are present.
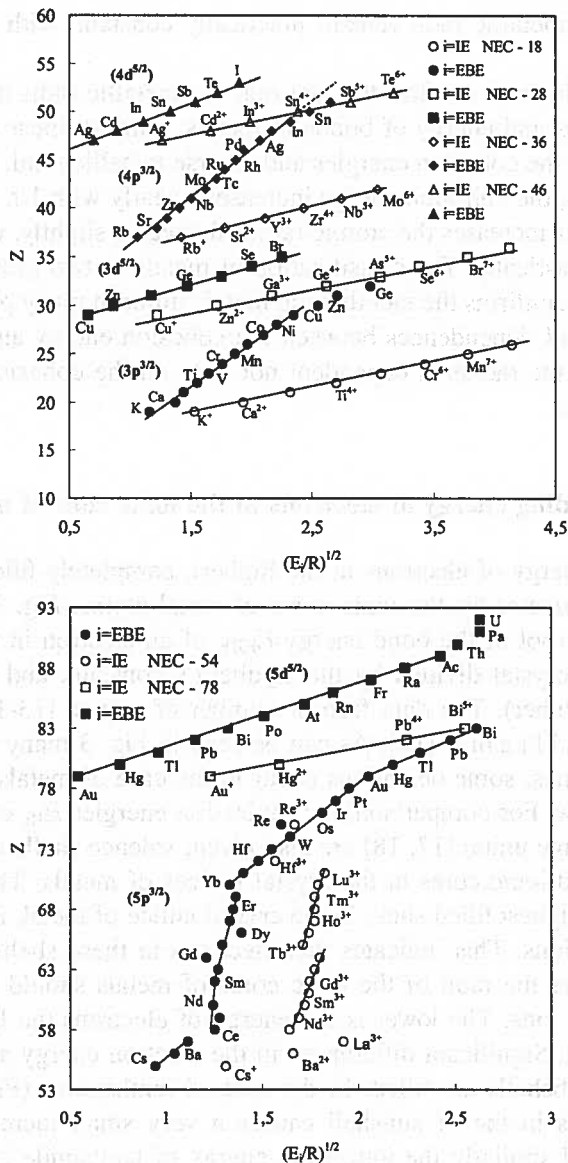
788

Fig. 3. Corelation between the charge of nucleus (Z) and square root of bonding energy of electrons in the last filled shell (E_{EBE})(full points)[13-16] and between the square root of ionization energy of ions (E_{IE}) with the same outer shells (empty points) in the Rydberg's units, (a) for metals with the last shell; row 3, $3p^{3/2}$ configuration, point – (●), $3d^{5/2}$ – (■), row 4; $4p^{3/2}$ – (♦), $4d^{5/2}$ – (▲), and ions: with 18 electrons – NEC-18 (number electron configuration) -(o), 28 – NEC-28 (□), 36 – NEC-36 (◇), 46 – NEC-46 (△), (b) for metals with the last shell row 5; $5p^{3/2}$ – (●) and $5d^{5/2}$ – (■) ions with 54 electrons NEC-54 (o), NEC-78 (□), as well as for lanthanides with valency 3+ (o)

In the light of the above-presented results, the bonding energy of electrons in the highest occupied shell of the ionic core should be inversely proportional to its radius and consequently it should be also a function of the metallic radius. Fig. 4 shows a correlation between the square root of the bonding energy of electrons in the highest p and d shells (divided by the Rydberg's constant) and the inverse metallic radius. It
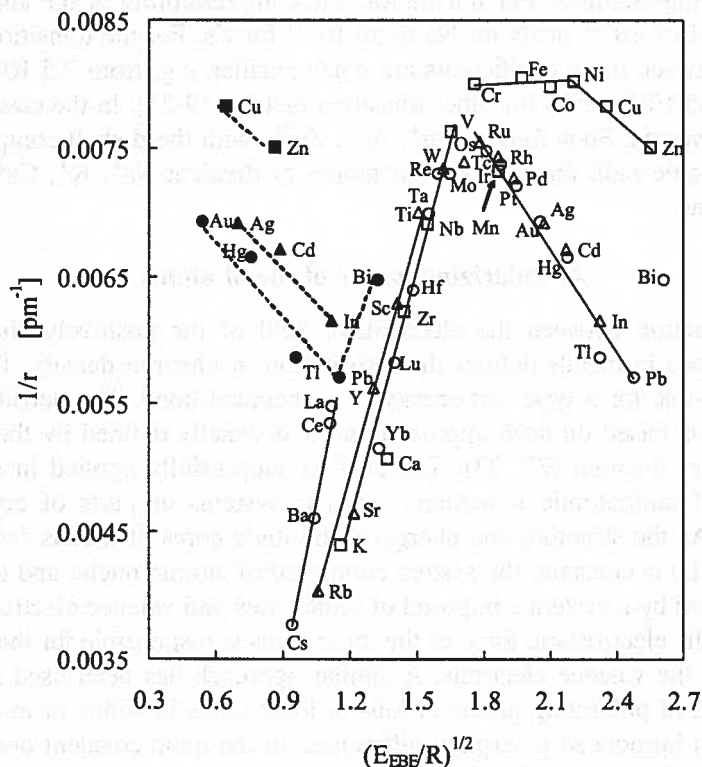

Fig. 4. Correlation between the inverse metallic radius and the square root of the bonding energy of electrons in the highest filled shell of the metallic core (in the Rydberg's units) row 3; $3p^{3/2}$ configuration, point – ($\square$) and ($3d^{5/2}$)($\blacksquare$), row 4; $4p^{3/2}$ – ($\triangle$) and $4d^{5/2}$ – ($\blacktriangle$), row 5; $5p^{3/2}$ – (o) and $5d^{5/2}$ – ($\bullet$)

can be noticed that the smaller is the atomic radius, the higher is the bonding energy of electrons in the last shell p. For the atoms which have more than 6 of d electrons, the bonding energy in the p subshell increases, while the atomic radius changes very slightly, as in the case of 3d metals (except Mn). As soon as the d subshell is filled up, the energy of electrons in the inner p shell increases despite the increasing atomic radius. The increase of the metallic radius begins already from Os and Ru, which do not have their d shells completely filled. The energy of electrons in the filled d shell of such elements as: Zn, Cd, In, Hg, and Tl is lower than the corresponding energy of the alkaline atoms. On the basis of Figs. 3 and 4, it can be stated that larger metallic radii

of Zn, Cd, Hg, In, and Tl should be related to d electrons because the low bonding energy of these electrons indicates significant increase of the ionic core /radius/. The quantum mechanics calculations for Cu, Ag and Au indicate that their d shells are relatively large and their radii are not much smaller than the metallic radii [19]. The d shells filled exert repulsive forces and this effect should contribute to the overall bond energy. This conclusion is confirmed by the atomic volume changes as a function of pressure or compressibility. For illustration, the compressibility of the alkaline metals changes from $14.7 \cdot 10^{-11}$ m^2/N for Na to $50 \cdot 10^{-11}$ for Cs. For the transition metals the differences between these coefficients are much smaller, e.g. from $2.5 \cdot 10^{-11}$ for Sc or Y to about $0.35 \cdot 10^{-11}$ m^2/N for other transition metals [19-21]. In the case of ions this tendency is reversed. Such ions as Cu^+, Ag^+, Zn^{2+}, with the d shell completely filled, have smaller ionic radii than the similar mono- or divalent Na^+, K^+, Ca^{2+}, Sr^{2+} ions in the same row.

4. Polarizing power of metal atoms

The interaction between the electrostatic field of the positively charged nuclei and the electrons in metals defines the distribution of electron density. This distribution is responsible for a type and energy of a chemical bond. The density functional theory (DFT) is based on such approach and it is exactly defined by the H o h e n - b e r g - K o h n theorem [22, 23]. The DFT is successfully applied in the quantum calculations of multiatomic structures, catalytic systems or parts of crystal lattices (300 atoms). As the structure and energy of the ionic cores of metals (with the filled electronic shells) is constant, the system composed of atomic nuclei and electrons can be approximated by a system composed of ionic cores and valence electrons. It can be assumed that the electrostatic force of the ionic cores is responsible for the distribution and energy of the valence electrons. A similar approach has been used in chemistry where a notion of polarizing power of ions or ionic cores in solids or in coordination complexes was introduced to explain differences in the ionic-covalent bonds. The polarizing power of an ion was first introduced by G o l d s c h m i d t, and it was defined as an energy of electrostatic field around a cation with a charge $+Z_c e$ and ionic radii r ($E = Z_c e/r^2$). Similar parameters are: electronegativity defined by A l l r e d - R o c h o w [24], the C a r t l e d g e ' s potential [25], electrostatic force of a cation defined by Ahrens [26], ionic core electronegativity defined by G ó r s k i - G o n t a r z [27], or the G ö r l i c h ' s electronegativity [28]. The ionization energy was used to determine the power of cations to exert electrostatic forces [26-28]. In the case of ionic cores of metals, the bonding energy of electrons in the outer shell might be a good parameter. When it is assumed that the radius of the ionic core is proportional to the metallic radius, the ratio of square root of the bonding energy of electrons of the ionic core (proportional to the charge) and the metallic radius, can be taken as a measure of the polarizing power of metal atoms P_M:

$$P_M = \frac{\sqrt{E_{EBE}/R}}{r/a_o}. \tag{1}$$

To obtain dimensionless values of the above parameters E_{EBE} was divided by the Rydberg's constant R and the radius r by radius of the first Bohr orbit of the hydrogen atom a_o. Thus defined parameter can be interpreted as an electrostatic force of the ionic core or as a potential generated by the ionic core. Fig. 5 shows the values of parameter
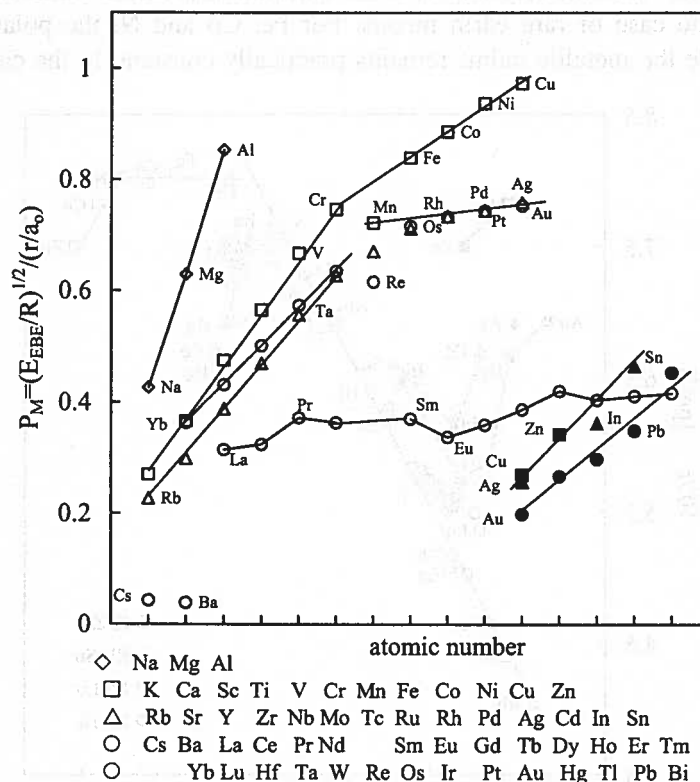

Fig. 5. Dependence of P_M – polarizing power of metal atoms in their crystals on the atomic number. P_M values for the ionic cores: row 3; $3p^{3/2}$ configuration, point – ($\square$) and $3d^{5/2}$ – ($\blacksquare$), row 4; $4p^{3/2}$ – ($\triangle$) and $4d^{5/2}$ – ($\blacktriangle$), row 5; $5p^{3/2}$ – (o) and $5d^{5/2}$ – ($\bullet$)

P_M vs. atomic number (the charge of nucleus) in different rows. For Cu, Ag and Au two values are given, corresponding to the ionic core with shell $p^{3/2}$ (open points) and, because of lacking E_{EBE} data for shell $d^{5/2}$, the values obtained from extrapolation of the data for metals of groups 12-15 with the d shells filled in the corresponding rows (Fig. 3). It can be stated that the values of parameter P_M, for the metals of the same row (groups 1-6) increase proportionally to the nucleus charge. Metals of group 7 (Mn, Tc, Re) deviate slightly from this rule what is also reflected in many other properties. The straight lines in Fig. 5 have different slopes for groups 8-10. The P_M values for the 4d and 5d metals are very similar whereas for the 3d metals — significantly higher. For the rare earth metals the P_M values are between those for La and Lu, they are small and do not differ much, in similar way as their sublimation enthalpy and metallic radii.

Relatively low P_M values are noted for the ionic cores of metals in groups 11- 15. Their highest electron shell filled is $d^{5/2}$. Table 1 presents the P_M values for elements that form crystal structures with metallic and covalent bonds.

Fig. 6 shows a dependence between inverse metallic radius and parameter P_M [11, 12]. For the elements of groups 1-5 the correlation is linear. Some deviations are observed in the case of rare earth metals. For Fe, Co and Ni the polarizing power increases while the metallic radius remains practically constant. In the case of 4d and
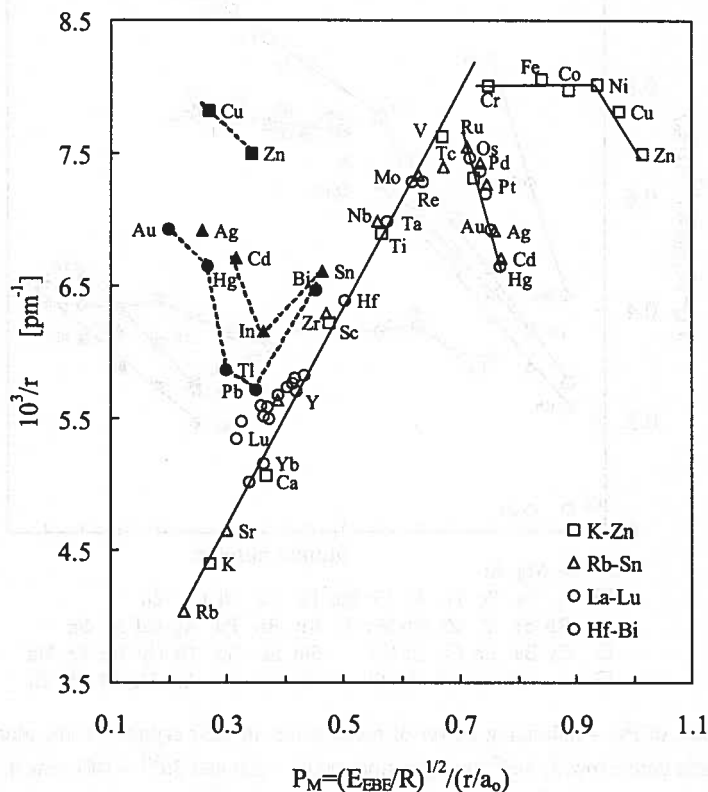

Fig. 6. Correlation between inverse metallic radius and P_M, P_M values for the ionic cores row 3; $3p^{3/2}$ configuration, point – ($\square$) and $3d^{5/2}$ – ($\blacksquare$), row 4; $4p^{3/2}$ – ($\triangle$) and $4d^{5/2}$ – ($\blacktriangle$), row 5; $5p^{3/2}$ – (o) and $5d^{5/2}$ –($\bullet$)

5d metals (group 8-10) the polarizing power increases slightly and the metallic radius also increases slightly. For the metals of group 11 and 12 it should be assumed that the metallic radius is dependent on ionic cores with the $p^{3/2}$ shell filled. Metals with the d shells filled (groups 13-15), in turn, have somewhat larger radii than metals with the $p^{3/2}$ shell filled but similar values of the P_M parameter. As the bond energy is a complex function of the metallic radius, a similar complex dependence should be expected between the polarizing power and the cohesion energy of metals. Fig. 7 presents a dependence between the sublimation enthalpy [9, 10] and the polarizing

power of metals. Almost linear correlations can be observed for several groups of metals. For the metals of groups 1-5, the bond energy increases with the polarizing power, while for metals of other groups the cohesion energy markedly decreases in spite of the increasing polarizing power.
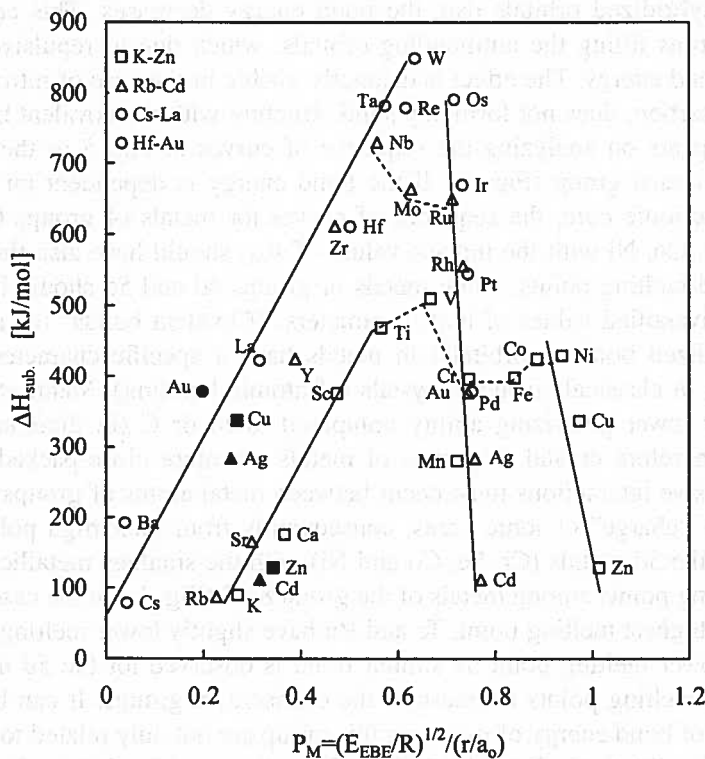

Fig. 7. Correlation between the sublimation enthalpy (ΔH_{sub}) and P_M. P_M values for the ionic cores: row 3; $3p^{3/2}$ configuration, point – ($\square$) and $3d^{5/2}$ – ($\blacksquare$), row 4; $4p^{3/2}$ – ($\triangle$) and $4d^{5/2}$ – ($\blacktriangle$), row 5; $5p^{3/2}$ – (o) and $5d^{5/2}$ – ($\bullet$)

Theories that describe the interactions in metals, the free electrons theory developed for the alkaline metals [19, 29] as well as the concepts of hybridized orbitals not completely filled with electrons developed for the transition metals [1-4], permit calculation of the bond energy and explanation of the coordination number of metals, spatial distribution of the orbitals. However, complexity of these descriptions makes difficult any explanation of the differences in properties of metals, as it was earlier stated by Wigner and Seitz [30]. Analyzing the data of bond energy and metallic radius (Figs. 1, 2) and the values of polarizing power (Figs. 5-7), the following remarks can be made. The electrons of the ionic cores of the alkaline metals have low bonding energy and therefore their metallic radii are relatively large, and the bond energy of these metals is low. As the number of d electrons and their contribution in the hybridized orbitals

dsp increase, the bond energy increases and therefore metals of groups 5 and 6 have the highest melting points. The large polarizing power of these metals are therefore responsible for the formation of strong covalent bonds, like in the case of classical covalent crystals as diamond, or SiC. For metals located more to the right (group 5 and next), in spite of the growing number of electrons, which should result in an increased energy of hybridized orbitals dsp, the bond energy decreases. This can be ascribed to the electrons filling the antibonding orbitals, which due to repulsive interact ions lower the bond energy. The effect is distinctly visible in the case of nitrogen, which, in contrast to carbon, does not form any solid structure with the covalent bonds. Another question appears on analyzing the sequence of curves in Fig. 5 or the melting point variations in each group (Fig. 1). If the bond energy is dependent on the polarizing power of the ionic core, the sequence of curves for metals of groups 6-10 would be reversed. Fe, Co, Ni with the highest values of P_M, should have also the highest bond energies and melting points, while metals of groups 4d and 5d should have lower and not much diversified values of both parameters. "Covalent bonds" (of not completely filled hybridized bonding orbitals) in metals have a specific character compared to the bonding in classical covalent crystals (of atomic bonding). Metal atoms have also significantly lower polarizing ability compared to Si or C (in diamond) atoms (see Table 1). Therefore crystal structures of metals are more close-packed. Accordingly, strong repulsive interactions must occur between metal atoms of groups 7-10 resulting from a high "charge" of ionic cores, consequently from their high polarizing power. Due to this the 3d metals (Cr, Fe, Co and Ni) with the smallest metallic radii have the lowest melting points among metals of the group 8-10 (Fig. 1). In the case of 4d metals, Mo has the highest melting point, Tc and Ru have slightly lower melting points and Pd has much lower melting point. A similar trend is observed for the 5d metals: starting from W the melting points decrease in the consecutive groups. It can be noticed that the changes of bond energy of metals in this group are not only related to the increasing metallic radius but these depend significantly on the repulsive interactions between the metal atoms, i.e. on their polarizing power. In the case of metals of group 11 due to the completely filled d shells, the polarizing power should be small. However, these metals differ largely from the alkaline ones because d electrons participate in the formation of bonding orbitals. Therefore the polarizing power of Cu, Ag and Au are higher than ones ascribed to ionic cores $d^{3/2}$, but they should be smaller than ones calculated for shells $p^{3/2}$. The effect of repulsive interactions is quite complex, particularly in the case of metals of groups 8-10 because their ionic cores cannot be limited to the filled p shells. It follows from the magnetic measurements and quantum mechanics calculations that not all d electrons are involved in the formation of bonds. After P a u l i n g [32], among the 3d metals, starting from Cr the contribution of bonding orbitals amounts to 5.78 from among 10 dsp orbitals available. Some of the orbitals are non-bonding and some are indispensable for maintaining the unsynchronized resonance between the bonding orbitals. The occurrence of the filled and the unfilled non-bonding orbitals indicates that the electrons occupying the latter should reduce the repulsive electrostatic

Polarizing power values P_M for the ionic cores in the thermodynamically stable states

Element	E_{EBE} [kJ/mol]	P_M	r [pm]	Element	E_{EBE} [kJ/mol]	P_M	r [pm]
Ag(p)	5625.08	0.759	144.4	Mg	4748.03	0.630	159.8
Ag*(d)	642.91	0.356	144.4	Mn	4554.09	0.722	136.5
Al.	6995.16	0.854	143.1	Mo	3425.22	0.628	136.2
Au(p)	5518.94	0.753	144.2	Na	2942.79	0.427	185.8
Au*(d)	382.59	0.198	144.2	Nb	2971.74	0.557	142.9
B	18139.18	3.585	54.8	Nd	2035.83	0.363	181.4
Ba	1427.98	0.039	217.3	Ni	6387.31	0.937	124.6
Be	10758.08	1.361	111.3	Os	4293.58	0.716	133.7
Bi	2296.34	0.453	154.5	Pb	1746.38	0.349	175.0
C	27421.04	3.393	1.3	Pd	4911.09	0.744	137.5
Ca	2450.72	0.366	197.3	Pr	2151.62	0.372	182.0
Cd	1032.39	0.315	148.9	Pt	4988.27	0.744	138.7
Ce	1640.25	0.324	182.5	Rb	1476.22	0.227	247.5
Co	5779.45	0.886	125.3	Re	3338.38	0.616	137.0
Cr	4071.67	0.746	124.9	Rh	4563.74	0.734	134.5
Cs	1167.47	0.043	265.4	Ru	4168.15	0.712	132.5
Cu(p)	7246.02	0.973	127.8	Sc	2730.53	0.475	160.6
Cu*(d)	554.32	0.269	127.8	Si	9571.31	1.215	117.6
Dy	2537.56	0.420	175.1	Sm	2055.13	0.370	178.9
Er	2383.18	0.411	173.4	Sn	2305.99	0.464	151.1
Eu	2122.67	0.337	199.4	Sr	1939.35	0.299	215.1
Fe	5084.76	0.839	124.1	Ta	3155.06	0.574	143.0
Ga	1804.27	0.508	122.1	Tb	2180.56	0.387	176.2
Gd	1929.70	0.359	178.6	Tc	3849.75	0.671	135.1
Ge	2817.36	0.633	122.5	Ti	3145.41	0.566	144.8
Hf	2884.90	0.502	156.3	Tl	1206.06	0.298	170.4
Hg	752.58	0.267	150.2	Tm	2412.13	0.416	172.3
Ho	2325.29	0.404	174.3	V	3589.24	0.668	131.1
In	1630.60	0.363	162.5	W	3550.65	0.635	137.0
Ir	4631.28	0.733	135.7	Y	2228.80	0.388	177.5
K	1765.68	0.270	227.2	Yb	2325.29	0.363	194.0
La	1620.95	0.315	186.9	Zn	974.50	0.342	133.2
Li	5277.73	0.698	151.9	Zr	2614.74	0.470	158.9
Lu	2576.15	0.432	171.7				

* – extrapolated values

(p) – P_M value for the last inner subshell p

interactions and therefore the polarizing power metals of groups 8-10 should be lower in comparison with ones calculated for the $p^{3/2}$ shells. It should be expected that for different metals of groups 8-10 the values of parameter P_M can deviate from the proposed ones. In general it can be stated that the polarizing power and changes of the metallic radii account for properties of metals, especially of those metals, which are located in the same row of the periodic table. It should be emphasized, however, that the proposed parameter P_M does not fully describe the magnitude of the ionic core potential, because it refers to the metallic radius and not to the radius of the ionic core itself. Moreover, it does not include the effects of the non-bonding d-electrons mentioned earlier, which reduce the repulsive electrostatic interactions. Nevertheless it is helpful in predicting the trends of property changes of metals. The polarizing power of metal atoms will particularly affect the properties of heteroatomic compounds with mixed metallic-ionic and metallic-covalent bonds, i.e. when the values of P_M differ significantly. The polarizing power of metal atoms will influence the properties of solid solutions and interstitial compounds with non-metals, such as nitrogen (N), hydrogen (H) or carbon (C).

5. Properties of hydrides, nitrides and carbides and the polarizing power of metal atoms

It follows from Fig. 5, that the alkaline metals and rare-earth metals, having low polarizing power, essentially do not dissolve H, N or C. They form ionic compounds instead, in which the mentioned non-metals accept electrons from the metallic elements and become negative ions. The typical ionic properties of these compounds are discussed in detail in numerous chemistry and crystallochemistry books e.g. [33, 34]. Mg, lanthanides and the mentioned non-metals form compounds characterized by mixed-type bonds with a remarkable contribution of the ionic component. Metals with higher polarizing power deserve special attention.

5.1. Interstitial hydrides

Because of great importance of the transition metal hydrides, the relevant bibliography is very rich [35-38]. The transition metal hydrides can be classified in two groups. Hydrogen dissolves in metals of groups 3-5 and forms stable hydrides with a negative formation enthalpy (Pd is also in this group). The polarizing power of these metals increase with the group number. Metals of the second group: Cr, Fe, Co, Ni, Mo and W absorb small amounts of H with an endothermic effect. At low hydrogen pressures they form α phases being solutions of H in metals. At higher pressures some ordered phases may appear, in which H occupies the crystallographic voids: first the octahedral sites and then the tetrahedral sites. In this process the lattice parameter increases. These phases have defined crystallographic structures and are classified as nonstoichiometric compounds [39]. Transition metal hydrides differ significantly from the ionic hydrides. In the ionic structure of alkaline metal hydrides the H^- radius

is relatively large, 130-150 pm, while the cation radius is much smaller than that of the corresponding metal atom. Density of alkaline metal hydrides is by 20-40% higher than the density of respective metals. Ordered structures are formed for transition metal hydride, lattice rearrangement (change of symmetry) is often observed. The hydrides have larger molar volumes, up to 25% than the corresponding metals. The significant hydrogen solubility in Sc, Ti, V, Zr, Hf and the formation of their stable hydrides should be therefore related to the high polarizing power of these metals, leading to the formation of covalent bonds. Another favorable factor is the appreciable size of crystallographic voids, resulting from the relatively large radius of these metals. In the case of H dissolution in metals and the formation of interstitial hydrides this parameter should not be of much importance. Small hydrogen atoms whose covalent radius is estimated as about 30 pm, should easily enter even in small tetrahedral voids. However, due to the increased electron density around proton more space may be required for H atom. Starting from metals of group 6, the solubility of H becomes low and hydrides of such metals as Cr, Mn, Fe or Pd are formed at high pressures. These metals have small radii (see Figs. 6 and 7) and it can be easily calculated that the size of voids becomes insufficient. However, these metals have the lowest bond energies among all transition metals and therefore dissolution of H can be accompanied by lattice expansion. Similar expansion is not possible in the case of refractory metals 4d, 5d (Os, Ir, Pt, Ru, Rh). The cohesion energy of these metals is so high that they do not form hydrides and exhibit very low solubility of H in spite of high polarizing power and the radii larger than those of the 3d metals.

5.2. Interstitial nitrides and carbides

Transition metals are also known to dissolve significant amounts of N or C and to form nitrides or carbides classified as interstitial compounds. Transition metals can be divided into two groups, by similarity to the hydrides. Figs. 8 and 9 present melting points of selected metals (full points) and the corresponding carbides and nitrides [7] (empty points). Carbides and nitrides of metals belonging to groups 4 and 5 have very high melting points, exceeding those of the corresponding metals, and their reactivity is very low. The extremely high melting points reflect the presence of strong covalent bonds, in which N or C plays an important role. These compounds are characterized by high electrical conductivity, similar to the electrical conductivity of the corresponding metals. As follows from Figs. 8 and 9, the nitrides and carbides of metals from groups 6-10, classified as interstitial compounds, have already much lower melting points. The melting points of Cr compounds are somewhat lower than of Cr itself, while MoN and WN decompose at temperatures lower than 1050 K. Metals located at the right side in the periodic table exhibit much lower solubility of C and only the 3d metals form carbides. Carbon atoms occupy progressively the interstitial sites in the close packed structures of metals, this is often accompanied by rearrangements of the original crystal structure of metal (A3 → A1 transformation). The carbide phases of metals from this group have lower melting points compared to pure metals and are less resistant to acids
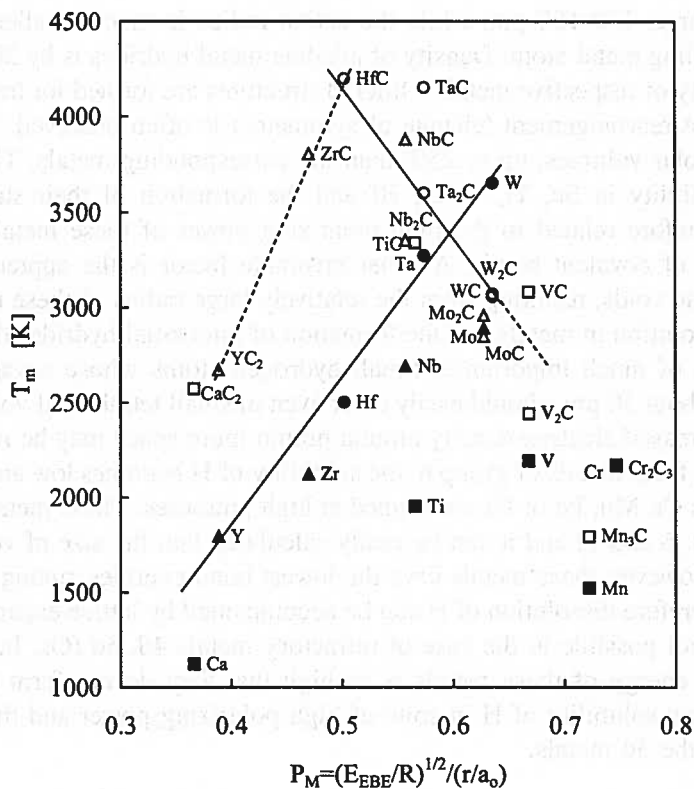
798

Fig. 8. Correlation between melting point of metals (full points) and their carbides [7] (empty points) and P_M values for the ionic cores: row 3; $3p^{3/2}$ configuration, point – (□), row 4; $4p^{3/2}$ – (△), row 5; $5p^{3/2}$ – (o)

(Fe$_3$C, Ni$_3$C) and to water (Mn$_3$C). The reaction products, in addition to H, contain mixtures of hydrocarbons, similarly to the ionic compounds of metals from groups 1 and 2. The most stable refractory metal carbides are: WC, RuC, OsC. The structural analyses undertaken by many authors [33] showed that the ratio of metal radius to non-metal radius was of importance. For instance the formation of d compound with the NaCl structure is possible when this ratio falls in a narrow range $0.41 < r_X/r_M < 0.63$ [40]. The structures of compounds with stoichiometries other than MX are dependent on the sequence of layers. It follows from this short review of the properties of the transition metal carbides and nitrides that structures with strong covalent bonds are formed when high polarizing power of metal atoms is accompanied by fulfillment of the geometrical requirements; it is similar to hydride phases. On the other hand, the solubilities of C and N are very limited in metals, in which the crystallographic voids are insufficient and the energy of metallic bond is high.
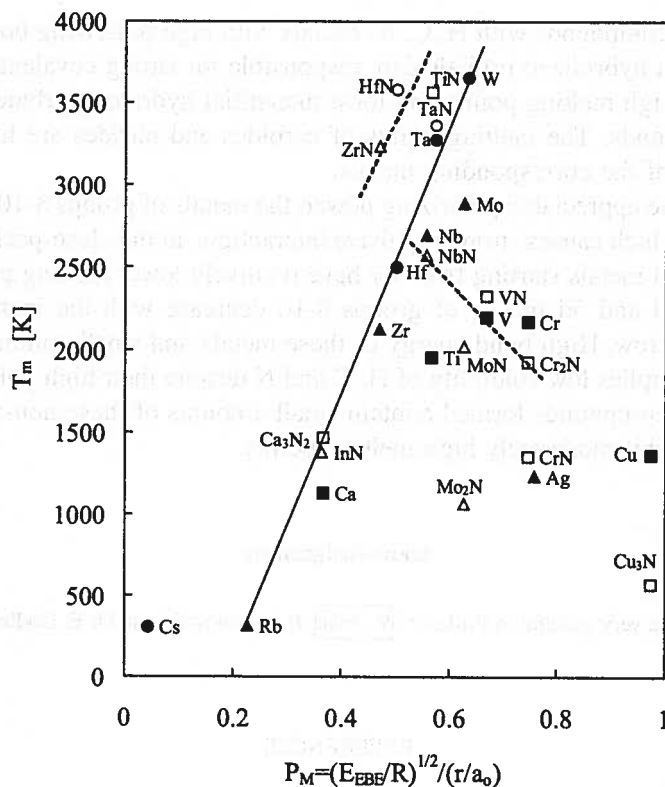
Fig. 9. Correlation between melting point of metals (full points) and corresponding nitrides [7] (empty points) and P_M value for the ionic cores: row 3; 3p3/2 configuration, point – (□), row 4; 4p3/2 – (△), row 5; 5p$^{3/2}$ – (o)

6. Conclusions

The dependence of the melting points of metals and the bonding energies of electrons on the inverse metallic radii indicate complex correlations between these parameters. Starting from the alkaline elements, which have the largest radii, the bonding energies of metals increase linearly with the inverse metallic radii until the d shell is half-filled. At higher number of electrons in atoms the bonding energy decreases linearly, with a larger slope than for the metals in groups 1-5.

The similar correlations are obtained for dependence of square root of the bonding energy of electrons in the outer shell of the ionic core of metals on the atomic number and on the inverse metallic radius. It indicates that this parameter can be used for characterizing atoms of metals.

The parameter of the polarizing power of metal atoms defined in equation (1), enables classification of atoms in terms of electrostatic interactions. Metals with low polarizing power (alkaline metals, rare-earth metals) show relatively low bond energies

and form ionic compounds with H, C, N. Metals with high polarizing power located in groups 3-6 form hybridized orbitals dsp, responsible for strong covalent bonds. These metals exhibit high melting points and form interstitial hydrides, carbides and nitrides with covalent bonds. The melting points of carbides and nitrides are higher than the melting points of the corresponding metals.

Owing to the appreciable polarizing power, the metals of groups 8-10 have relatively small radii, which causes strong repulsive interactions in the close-packed structures. Therefore the 3d metals starting from Cr have relatively lower melting points. Melting points of the 4d and 5d metals of groups 8-10 decrease with the increasing atomic number in each row. High bond energy of these metals and small volume of crystallographic voids implies low solubility of H, C and N despite their high polarizing power. The interstitial compounds formed contain small amounts of these non-metals and the compounds exhibit moderately high melting points.

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