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New Relation between Ionic Radii, Bond Length, and Bond Strength

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Based on the table of the effective ionic radii of R. D. Shannon (*Acta Crystallogr. Sect. A* **32,** 751, 1976), the linear relation of the cationic radii on the coordination number k has been observed:

$$r_k = r_0 + dk - \frac{0.0236\,k}{z},$$

where r_0 is the radius of free cation, z its valence, and $d = 0.1177 - 0.0081\,z - 0.0347\,r_0 - 0.0050\,zr_0$. The analogous relation for O^{2-} anion has been found to be $r'_{k'} = r'_0 + a'k' = 1.328 + 0.0118\,k'$. By adding r_k and $r'_{k'}$ corresponding to the same bond strength new dependence between bond length R and bond strength s has been established for cation–oxygen bonds:

$$s = \frac{dz}{R - R_0},$$

where $R_0 = r_0 + r'_0$. The necessity to choose a standard state for ionic radii and for bond strength is pointed out and argued. Structures of simple oxides at room temperature and at normal pressure are chosen as standard state at which the sum of the strengths of bonds around the cation is assumed to be exactly equal to its z. *Standard radii of free ions* r_0 are determined for about 230 ions and are listed. As in Shannon's table some ionic radii were found to be negative. Physical sense can be hardly attributed to this finding. To avoid the negative radii a new scale of *absolute ionic radii* ρ_0 is proposed, based on assumption that $\rho_0(H^{1+}) = 0$ instead of $r_0(H^{1+}) = -h = -0.499$ (the size of the proton is known to be of the order of 10^{-5} Å, i.e., much less than the accuracy of determination of ionic radii). Consequently ρ_0 for all cations is assumed to be $\rho_0 = r_0 + h$ and for anions $\rho'_0 = r'_0 - h$ (e.g., $\rho'_0(O^{2-}) = 0.829$ Å). Bond-length–bond-strength relationship expressed by the equation indicated above is rationalized in terms of the new proposed *electrostatic hover model* of crystal structure. In this model ions are of constant size (r_0 or ρ_0), they do not touch each other, but they are maintained at distances $L = R - R_0$ by the electrostatic forces. This remains in agreement with the suggested (J. Ziółkowski, *J. Catal.* **84,** 317, (1983)) linear relation between bond strength and bond energy $E = Js$ which will be proved in the forthcoming paper (J. Ziólkowski and L. Dziembaj, *J. Solid State Chem.* **57,** 291 (1985)).

Introduction

The concept of the electrostatic bond strength, s, was defined by Pauling (*1*) as the valence of cation z divided by its coordination k:

$$s = \frac{z}{k} \tag{1}$$

As follows from the definition

$$\sum_1^k s_i = z. \tag{2}$$

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Pauling stated that in a stable ionic structure also the valence of each anion z' (all parameters concerning anion will be indexed throughout this paper with "prime") is exactly (or nearly) equal to the sum of the strengths of the bonds to it from the adjacent cations:

$$\sum_{1}^{k'} s_i = z'. \tag{3}$$

Deviations from Pauling's rule were usually interpreted by stating that bond strength must depend on the anion–cation distance R. As reviewed by Brown (*2*) various empirical methods for calculating cation–oxygen bond strength as a function of bond length have been proposed so far, two of which having become widely applicable and accepted; the inverse power function

$$s = \left(\frac{R}{R_1}\right)^{-N} \tag{4}$$

and the exponential function

$$s = \exp\left(\frac{R - R_1}{B}\right), \tag{5}$$

where s is the bond strength expressed in valence units (vu) and R is the bond length expressed in Ångstroms. R_1, N, and B are empirical parameters determined for about 120 cations (*2–6*). The concept of the bond strength can also be used in the situation where the binding is primarily covalent (*3*) and thus the terms "cation" and "anion" are still used for convenience only.

Although bond strengths calculated with Eqs. (4) or (5) have a number of practical applications in the analysis of crystal structures (*2*), it should be stressed that the form of these equations has never been rationalized. Since the bond strength has an electrostatic origin one could expect that s–R dependence should rather have a coulombic form

$$s = \frac{\text{const}}{R} \tag{6}$$

with the bond strength proportional to the bond energy

$$E = Js \tag{7}$$

The E–s relationship expressed by Eq. (7) has been demonstrated for the first time for C–O bonds in CO_2 and in various organic molecules (*7*). Its validity for inorganic solids will be examined and confirmed in a forthcoming paper (*8*), aiming at formulation of a general bond-length–bond-strength–bond-energy concept.

However, Eqs. (6) and (7) on one hand and Eqs. (4) and (5) on the other, do not combine well. For example, by combining Eqs. (4) and (7) we have

$$E \sim \frac{1}{R^N} \tag{8}$$

with N varying between 2.2 and 9 and being $4.5 \leq N \leq 7$ for the majority of studied cations (*2, 4*). This is a rather paradoxical conclusion because such high powers are usually considered as characteristic of interactions resulting from various types of dispersion forces and not from electrostatic interactions, the predominating component of the lattice energy.

On the other hand, Eq. (4) applied to structures with equal lengths of all bonds and thus combined with Eq. (1) may be easily transformed to

$$R = R_1 \left(\frac{k}{z}\right)^{1/N}, \tag{9}$$

which makes it possible to determine the dependence of the cation–oxygen distance on the coordination number. However, R–k dependences calculated in such a way frequently disagree with those calculated from effective ionic radii (*9, 10*). Some examples are shown in Fig. 1.

In view of the above comments it seems that Eqs. (4) and (5), although convenient are (in view of their form) only an approximation in which the physical sense has

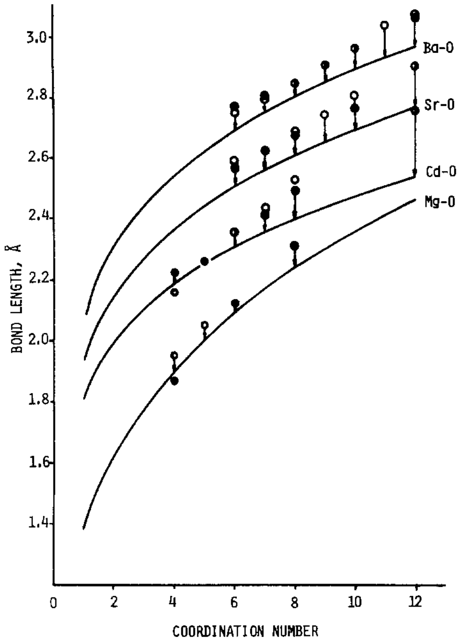

FIG. 1. Bond lengths of some Me^{2+}–O bonds at various coordinations resulting from the bond-length–bond-strength relationship (Eq. (4), lines) and from the table of the effective ionic radii of Shannon and Prewitt (black points) or of Shannon (open points). The latter are calculated by adding the ionic radii of cation and O^{2-} at the same coordination. Lacking radii of O^{2-} were determined by interpolation or extrapolation (cf. Fig. 2).

been lost. Therefore searching for a more rationalized s–R function seems to be substantiated.

Let us note moreover that once it has been decided that s must depend on R, the rule expressed by Eqs. (2) and (3) cannot be valid in general. If a given crystal is heated, the bond lengths increase, their strengths decrease and Σs_i becomes smaller and smaller. The opposite effect is expected if two simple oxides react to form a thermodynamically more stable mixed oxide or salt. It therefore seems obvious that a choice of a standard state for s (and so for ionic radii, being the components of the bond length) is necessary.

The above-mentioned problems will be discussed in detail in this paper. A new s–R equation will be proposed. It will be indicated how to make consistent the parameters for calculating cation–oxygen bond strength and the values of ionic radii. E–s–R relationship will be treated in the forthcoming paper (*8*). In searching the s–R function two approaches will be considered. They do not differ essentially in their general idea, but in some details of mathematical description. The second approach is considered to reflect better the nature of the discussed problems.

First Approach to the s–R Relationship

(*I*) *Dependence of Ionic Radius on Coordination*

The present considerations use the effective ionic radii compiled by Shannon (*10*). Those radii based upon the empirical bond-length–bond-strength relationship (Eq. (4)) which was questioned in the Introduction, are eliminated from the considered set. Consequently the radii determined by Shannon and Prewitt (*9*) are used for Ag^{1+}, Ba^{2+}, Bi^{3+}, Ca^{2+}, Cd^{2+}, Cs^{1+}, La^{3+}, Pb^{2+}, and Sr^{2+}.

The tables (*9, 10*) contain 58 cations (mentioned in Fig. 3) for which the effective ionic radii r_k were determined for at least three different coordinations. It appears that for all these ions a linear r_k–k dependence is observed:

$$r_k = r_0 + ak, \qquad (10)$$

where r_0 is the extrapolated radius of the free ion ($k = 0$). Selected examples are shown in Fig. 2. The straight lines were determined with the least-squares method and the correlation coefficients c were greater than 0.999 for 26 of the cations, 0.995 for 18 cations, 0.990 for 9 cations, 0.98 for 4 cations, and equal to 0.956 for one cation (Hg^{2+}). Equation (10) is also valid for O^{2-} ($c = 0.993$):

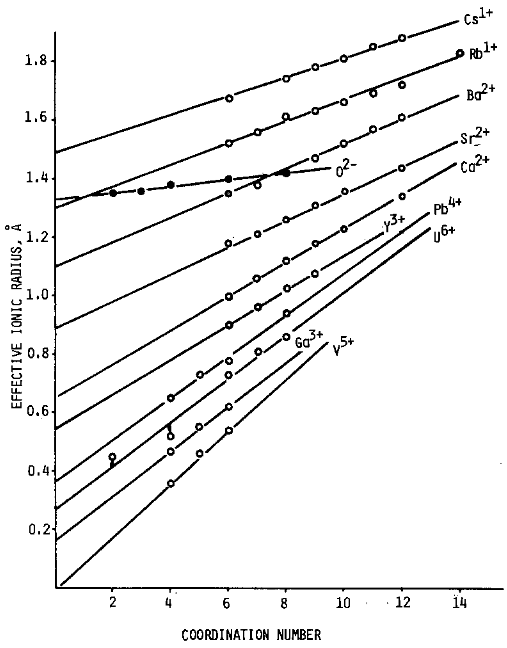

FIG. 2. Selected examples of the linear dependence of the effective ionic radius on coordination number.

$$r'_{k'} = r'_0 + a'k' = 1.328 + 0.0118k' \quad (11)$$

and for F^{1-} ($c = 0.995$)

$$r'_{k'} = 1.265 + 0.0110k'. \quad (12)$$

In this paper all numerical data are given with exaggerated accuracy to avoid the error of rounding in further calculations; radii and lengths are expressed in Ångstroms.

As the 60 ions indicated above are of various valences and electronic structure and are dispersed over the entire periodic table it seems that they form a representative set. Consequently one can postulate that Eq. (10) is valid for all ions of all the elements.

As shown in Fig. 3 the parameters r_0 and a in Eq. (10) are not independent, but they fulfill the linear relation

$$a = a_0 - br_0 = 0.0811 - 0.0379\, r_0. \quad (13)$$

Combining Eqs. (10) and (13) we receive

$$\begin{aligned} r_k &= (1 - kb)r_0 + a_0 k \\ &= (1 - 0.0379k)r_0 + 0.0811k. \quad (14) \end{aligned}$$

From Eq. (14) we see that r_k for a given cation depends on only one parameter r_0 characteristic of this ion.

It is true that the correlation for Eq. (13) is rather poor (0.889) but let us remark that r_k is usually strongly dependent on r_0 and only slightly on a. Thus even a large absolute error of a results in a small error of r_k. To evaluate the validity and precision of the generalized r_k–k dependence expressed by Eq. (14) two subsidiary dotted lines are drawn in Fig. 3 at distances ±0.01 from the solid line determined with the least-squares method. If a point in Fig. 3 for a given ion lay on one of the auxiliary lines, its r_k at the most common coordination $k = 6$, resulting from Eq. (14), was larger or smaller by 0.06 Å from that ($r_{6,S}$) determined by Shannon (*10*). As results from Fig. 3, the differences ($r_k - r_{k,S}$) are much smaller for the majority of considered cations and comparable with an error of empirical determination of ionic radii. There are only three ions which do not fit the linear a–r_0 relationship (Mo^{6+}, Cr^{5+}, Ta^{5+}). This may be due to the fact that these ions form usually strongly distorted structures, which markedly influences the precision of r_k determination (*10*). It will be shown further, in favor of the above supposition, that Mo^{6+} ion "forced" to lie on the a–r_0 line (or on the d–r_0 line in terms of the second approach) gains a quite good s–R dependence, especially in terms of the second approach (cf. Fig. 9 and Table III).

(II) Relation between Bond Length and Bond Strength

Making use of Eq. (10) one can calculate the bond length R between a cation of valence z and O^{2-} anion of $z' = 2$, corresponding to a chosen bond strength[1]:

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[1] The concept of the spherical ions contains the premise that idealized structures are considered, for which Eqs. (15) and (16) are adequate. In such structures k, k', R, and s change by steps. In particular we deal with a number of corresponding pairs of values (s_i, R_i). These points, marked in the s–R coordinates, trace a general s–R relationship (with s and R changing fluently), as expressed by Eqs. (17), (20), and (21).

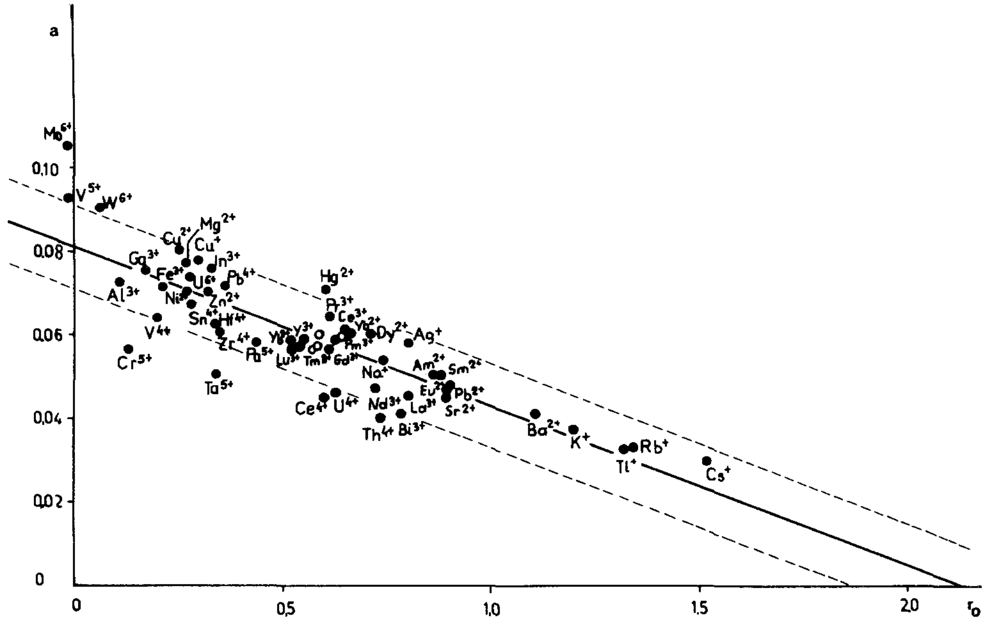

FIG. 3. Dependence between parameters a and r_0 from Eq. (13) (first approach). Open points at about $r_0 = 0.6$ and $a = 0.06$ represent the overlapping data for Ca^{2+}, Cd^{2+}, Dy^{3+}, Er^{3+}, Eu^{3+}, Ho^{3+}, Sm^{3+}, and Tb^{3+}. Solid line is determined with the least-squares method. Auxiliary dotted lines serve to evaluate the precision of the a–r_0 dependence (as discussed in text).

$$s = \frac{z}{k} = \frac{2}{k'}. \tag{15}$$

For this purpose one has to sum r_k corresponding to $k = z/s$ and $r'_{k'}$ corresponding to $k' = 2/s$:

$$R = r_0 + \frac{za}{s} + r'_0 \frac{2a'}{s}. \tag{16}$$

Transforming Eq. (16) one arrives at

$$s = \frac{za + 2a'}{R - r_0 - r'_0}. \tag{17}$$

Let us introduce

$$R_0 = r_0 + r'_0 \tag{18}$$

$$R^1 = r_z^1 + r_2'^1, \tag{19}$$

where R^1 is the bond length expected for a bond of unit valence, which obviously takes place if $k = z$ and $k' = 2$. As is evident from Eqs. (17), (18), and (19):

$$s = \frac{R^1 - R_0}{R - R_0}. \tag{20}$$

Equation (20) may be considered as a general dependence between the bond strength and the bond length alternative to Eqs. (4) and (5) and drawn upon only one well-argued assumption of the linearity of the r_k–k dependence. There are two parameters in this equation (R_0 and R^1) which could be fitted for each ion in a manner analogous to that applied in earlier works (*3, 4*).

If, however, we make use of Eqs. (13) and (14), Eqs. (17) and (20) transform to

$$s = \frac{az + 2a'}{R - R_0} = \frac{za_0 - zbr_0 + 2a'}{R - r_0 - r'_0} = \frac{0.0811z - 0.0379zr_0 + 0.0236}{R - r_0 - 1.328}, \tag{21}$$

where there is only one parameter r_0 to be fitted. As r_0 is also the only parameter determining r_k values, r_k–k (Eq. (14)) and s–R (Eq. (21)) relationships can be fitted simultaneously.

From Eqs. (20) and (21) we also see that the bond strength is proportional to the re-

TABLE I

STANDARD RADII OF FREE IONS (r_0), ABSOLUTE IONIC RADII (ρ_0), AND STANDAD IONIC RADII AT k-FOLD COORDINATION r_k COMPARED WITH EFFECTIVE IONIC RADII $r_{k,S}$ DETERMINED BY SHANNON (*10*)

	First approach	Second approach				
Ion^a	r_0	r_0	ρ_0	$r_k{}^b$	$r_{k,S}$	Remarks^c
Ac^{3+}	0.820	0.864	1.363	→	1.12_6	E 6
Ag^{1+}	0.548	0.540	1.039	0.927_6	1.15_6	D (11) c
Ag^{2+}	0.548	0.530	1.029	0.926_6	0.94_6	E 4
Ag^{3+}	0.341	0.337	0.836	→	0.75_6	E 6
Al^{3+}	0.061	0.030	0.529	0.534_6	0.535_6	D (11) k
Am^{2+}	0.798	0.772	1.271	1.213_8	1.26_8	D (11) n
Am^{3+}	0.632	0.658	1.157	→	0.975_6	E 6
Am^{4+}	0.436	0.565	1.064	0.856_6	0.85_6	D (11) f
As^{3+}	0.121	0.095	0.594	→	0.58_6	E 6
As^{5+}	0.012	0.059	0.558	0.473_6	0.46_6	E 4
At^{7+}	0.173	0.471	0.970	→	0.62_6	E 6
Au^{1+}	1.144	1.121	1.620	→	1.37_6	E 6
Au^{3+}	0.470	0.479	0.978	→	0.85_6	E 6
Au^{5+}	0.108	0.210	0.709	→	0.57_6	E 6
B^{3+}	−0.211	−0.238	0.261	0.151_4	0.11_4	D (12)
Ba^{2+}	1.133	1.126	1.625	1.362_6	1.35_6	D (11) n
Be^{2+}	−0.060	−0.104	0.395	0.273_4	0.27_4	D (13)
Bi^{3+}	0.703	0.736	1.235	1.128_8	1.17_8	E 6
Bi^{5+}	0.359	0.506	1.005	→	0.76_6	E 6
Bk^{3+}	0.613	0.636	1.135	→	0.96_6	E 6
Bk^{4+}	0.404	0.524	1.023	0.828_6	0.83_6	E 8
Br^{1-}	1.892	1.892	1.393	→	1.96_6	E 6
Br^{3+}	0.313	0.309	0.808	→	0.59_4	E 4
Br^{5+}	0.075	0.112	0.611	→	0.31_3	E 3
Br^{7+}	−0.087	0.027	0.526	0.361_6	0.39_6	E 4
C^{2+}	−0.304	−0.316	0.181	-0.212_2	—	D (14) m
C^{4+}	−0.368	−0.378	0.121	-0.078_3	-0.08_3	D (14) m
Ca^{2+}	0.673	0.640	1.139	1.128_8	1.12_8	D (11) n
Cd^{2+}	0.599	0.562	1.061	0.949_6	0.95_6	D (11) n
Ce^{3+}	0.709	0.762	1.261	1.048_6	1.01_6	E 8
Ce^{4+}	0.457	0.591	1.090	0.873_6	0.87_6	D (11) f
Cf^{3+}	0.600	0.622	1.121	→	0.95_6	E 6
Cf^{4+}	0.433	0.512	1.011	0.923_8	0.92_8	E 6
Cl^{1-}	1.742	1.742	1.243	→	1.81_6	E 6
Cl^{5+}	−0.139	−0.119	0.380	→	0.12_3	E 3
Cl^{7+}	−0.288	−0.209	0.290	0.224	0.27_6	E 4
Cm^{3+}	0.626	0.650	1.149	→	0.97_6	E 6
Cm^{4+}	0.433	0.561	1.061	0.853_6	0.85_6	D (11) f
Co^{2+}HS	0.321	0.268	0.767	0.734_6	0.745_6	D (11) n
Co^{2+}LS	0.212	0.153	0.652	→	0.65_6	E 6
Co^{3+}HS	0.159	0.138	0.637	→	0.61_6	E 6
Co^{3+}LS	0.076	0.045	0.544	→	0.545_6	E 6
Co^{4+}HS	0.056	0.079	0.578	→	0.53_6	E 6
Cr^{2+}HS	0.406	0.358	0.857	→	0.80_6	E 6
Cr^{2+}LS	0.315	0.262	0.761	→	0.73_6	E 6
Cr^{3+}	0.171	0.150	0.649	0.618_6	0.615_6	D (11) k
Cr^{4+}	0.071	0.096	0.595	0.541_6	0.55_6	D (11) r

TABLE I—*Continued*

	First approach	Second approach				
Ion[a]	r_0	r_0	ρ_0	r_k[b]	$r_{k,S}$	Remarks[c]
Cr^{5+}	0.024	0.073	0.572	0.482_6	0.49_6	E 4
Cr^{6+}	−0.076	−0.001	0.498	→	0.26_4	E 4
Cs^{1+}	1.374	1.366	1.865	1.557_6	1.67_6	D (15)
Cu^{1+}	0.337	0.328	0.827	0.766_6	0.77_6	D (11) c
Cu^{2+}	0.255	0.221	0.720	0.700_6	0.73_6	D (11)
Cu^{3+}	0.069	0.038	0.537	→	0.54_6	E 6
D^{1+}	−0.284	−0.296	0.203	→	-0.10_2	E 2
Dy^{2+}	0.755	0.727	1.226	1.184_8	1.19_8	E 6
Dy^{3+}	0.553	0.571	1.070	0.914_6	0.912_6	D (16) b
Er^{3+}	0.519	0.533	1.032	0.887_6	0.890_6	D (17) b
Eu^{2+}	0.889	0.868	1.367	1.173_6	1.17_6	D (11) n
Eu^{3+}	0.596	0.618	1.117	1.056_8	1.066_8	E 6
F^{1-}	1.264	1.264	0.765	1.330_6	1.33_6	Eq. (12)
F^{7+}	−0.526	−0.457	0.042	→	0.08_6	E 6
Fe^{2+}HS	0.338	0.286	0.785	0.747_6	0.780_6	D (11) n
Fe^{2+}LS	0.160	0.098	0.597	→	0.61_6	E 6
Fe^{3+}HS	0.145	0.122	0.621	0.600_6	0.645_6	D (11) k
Fe^{3+}LS	0.082	0.052	0.551	→	0.55_6	E 6
Fe^{4+}	0.127	0.161	0.660	→	0.585_6	E 6
Fe^{6+}	−0.088	−0.014	0.485	→	0.25_4	E 4
Fr^{1+}	1.700	1.685	2.184	→	1.80_6	E 6
Ga^{3+}	0.170	0.156	0.655	0.623_6	0.620_6	D (18)
Gd^{3+}	0.584	0.605	1.104	1.048_8	1.053_8	E 6
Ge^{2+}	0.315	0.262	0.761	→	0.73_6	E 6
Ge^{4+}	0.038	0.059	0.558	0.516_6	0.530_6	D (11) r
H^{1+}	−0.493	−0.499	0.000	-0.393_1	-0.38_1	D (14) m
Hf^{4+}	0.274	0.364	0.863	0.721_6	0.71_6	D (11) f
Hg^{1+}	0.910	0.885	1.384	→	1.19_6	E 6
Hg^{2+}	0.690	0.659	1.158	1.141_8	1.14_8	E 6
Ho^{3+}	0.529	0.545	1.044	1.013_8	1.015_8	D (17) b
I^{1-}	2.132	2.132	1.633	→	2.20_6	E 6
I^{5+}	0.600	0.802	1.301	→	0.95_6	E 6
I^{7+}	0.056	0.316	0.815	0.458_4	0.42_4	E 6
In^{3+}	0.411	0.415	0.914	0.804_6	0.800_6	D (17) b
Ir^{3+}	0.250	0.237	0.736	→	0.68_6	E 6
Ir^{4+}	0.179	0.221	0.720	→	0.625_6	E 6
Ir^{5+}	0.108	0.210	0.709	→	0.57_6	E 6
K^{1+}	1.226	1.213	1.712	1.440_6	1.38_6	D (11) f
La^{3+}	0.706	0.739	1.238	1.129_8	1.16_8	E 6
Li^{1+}	0.298	0.278	0.777	0.578_4	0.590_4	D (11) f
Lu^{3+}	0.485	0.495	0.994	0.982_8	0.977_8	E 6
Mg^{2+}	0.286	0.231	0.730	0.707_6	0.720_6	D (11) n
Mn^{2+}HS	0.436	0.589	0.888	0.823_6	0.830_6	D (11) n
Mn^{2+}LS	0.237	0.180	0.679	→	0.67_6	E 6
Mn^{3+}HS	0.328	0.323	0.822	0.740_6	0.645_6	D (17) b
Mn^{3+}LS	0.121	0.095	0.594	→	0.58_6	E 6
Mn^{4+}	0.047	0.069	0.568	0.523_6	0.530_6	D (11) r
Mn^{5+}	0.007	0.053	0.552	→	0.33_4	E 4
Mn^{6+}	−0.082	−0.007	0.492	→	0.255_4	E 4

TABLE I—*Continued*

	First approach	Second approach				
Ion[a]	r_0	r_0	ρ_0	r_k[b]	$r_{k,S}$	Remarks[c]
Mn^{7+}	−0.088	0.026	0.525	→	0.25_4	E 4
Mo^{3+}	0.263	0.252	0.751	→	0.69_6	E 6
Mo^{4+}	0.204	0.250	0.749	0.644_6	0.650_6	D (19)
Mo^{5+}	0.160	0.223	0.722	0.578_6	0.61_6	E 4
Mo^{6+}	0.054	0.175	0.674	0.498_6	0.59_6	D (20)
N^{3-}	1.414	1.414	0.915	→	1.46_4	E 4
N^{3+}	−0.423	−0.504	−0.005	→	0.16_6	E 6
N^{4+}	−0.340	−0.349	0.150	0.202_6	—	D (14) m
N^{5+}	−0.490	−0.398	0.107	→	-0.104_3	E 3
Na^{1+}	0.773	0.756	1.255	1.092_6	1.02_6	D (11) f
Nb^{2+}	0.285	0.230	0.729	0.706_6	—	D (11) n
Nb^{3+}	0.302	0.294	0.793	→	0.72_6	E 6
Nb^{4+}	0.256	0.307	0.808	0.683_6	0.68_6	D (21)
Nb^{5+}	0.198	0.319	0.818	→	0.64_6	E 6
Nd^{2+}	0.920	0.890	1.389	→	1.29_8	E 8
Nd^{3+}	0.660	0.705	1.204	1.008_6	0.983_6	E 8
Ni^{2+}	0.257	0.201	0.700	0.685_6	0.690_6	D (11) n
Ni^{3+}HS	0.147	0.123	0.622	→	0.60_6	E 6
Ni^{3+}LS	0.095	0.066	0.565	→	0.56_6	E 6
Ni^{4+}LS	−0.009	0.005	0.504	→	0.48_6	E 6
No^{2+}	0.794	0.768	1.267	→	1.1_6	E 6
Np^{2+}	0.802	0.776	1.275	1.106_6	1.10_6	D (11) n
Np^{3+}	0.677	0.707	1.206	→	1.01_6	E 6
Np^{4+}	0.472	0.609	1.108	0.885_6	0.87_6	D (11) f
Np^{5+}	0.341	0.490	0.989	→	0.75_6	E 6
Np^{6+}	0.302	0.538	1.037	→	0.72_6	E 6
Np^{7+}	0.289	0.627	1.125	→	0.71_6	E 6
O^{2-}	1.328	1.328	0.829	1.399_6	1.40_6	Eq. (11)
Os^{4+}	0.185	0.228	0.727	→	0.630_6	E 6
Os^{5+}	0.114	0.218	0.717	→	0.575_6	E 6
Os^{6+}	0.076	0.252	0.751	→	0.545_6	E 6
Os^{7+}	0.050	0.308	0.807	→	0.525_6	E 6
Os^{8+}	0.077	0.272	0.771	→	0.39_4	E 4
P^{3+}	−0.060	−0.105	0.394	→	0.44_6	E 6
P^{5+}	−0.182	−0.157	0.342	→	0.17_4	E 4
Pa^{2+}	0.770	0.742	1.241	1.081_6	—	D (11) n
Pa^{3+}	0.716	0.750	1.249	→	1.04_6	E 6
Pa^{4+}	0.515	0.662	1.161	0.921_6	0.90_6	D (11) f
Pa^{5+}	0.380	0.537	1.036	0.862_8	0.91_8	E 6
Pb^{1+}	0.858	0.850	1.349	1.163_6	—	D (11) c
Pb^{2+}	0.704	0.688	1.187	1.042_6	1.19_6	D (11)
Pb^{4+}	0.373	0.444	0.943	→	0.775_6	E 6
Pd^{1+}	0.463	0.454	0.953	→	0.59_2	E 2
Pd^{2+}	0.483	0.440	0.939	→	0.86_6	E 6
Pd^{3+}	0.354	0.351	0.850	→	0.76_6	E 6
Pd^{4+}	0.166	0.206	0.705	→	0.615_6	E 6
Pm^{3+}	0.637	0.679	1.178	0.989_6	0.97_6	E 8
Po^{4+}	0.630	0.805	1.304	1.088_8	1.08_8	D (11) f
Po^{6+}	0.237	0.457	0.956	→	0.67_6	E 6

TABLE I—*Continued*

Ion[a]	First approach	Second approach				Remarks[c]
	r_0	r_0	ρ_0	r_k[b]	$r_{k,S}$	
Pr^{3+}	0.707	0.738	1.237	1.129_8	1.126_8	D (17) b
Pr^{4+}	0.494	0.635	1.134	0.992_8	0.96_8	D (11) f
Pt^{2+}	0.405	0.358	0.857	→	0.80_6	E 6
Pt^{4+}	0.179	0.221	0.720	→	0.626_6	E 6
Pt^{5+}	0.108	0.210	0.709	→	0.57_6	E 6
Pu^{2+}	0.768	0.741	1.240	1.080_6	—	D (11) n
Pu^{3+}	0.665	0.693	1.192	→	1.00_6	E 6
Pu^{4+}	0.449	0.581	1.080	0.867_6	0.86_6	D (11) f
Pu^{5+}	0.328	0.475	0.974	→	0.74_6	E 6
Pu^{6+}	0.289	0.522	1.022	→	0.71_6	E 6
Ra^{2+}	1.193	1.186	1.685	→	1.48_8	E 8
Rb^{1+}	1.380	1.369	1.868	1.622_8	1.61_8	D (11) f
Re^{4+}	0.185	0.228	0.728	→	0.63_6	E 6
Re^{5+}	0.121	0.226	0.725	→	0.58_6	E 6
Re^{6+}	0.037	0.203	0.702	0.515_6	0.55_6	D (11)
Re^{7+}	0.065	0.206	0.705	→	0.38_4	E 4
Rh^{3+}	0.230	0.216	0.715	→	0.665_6	E 6
Rh^{4+}	0.147	0.183	0.682	→	0.60_6	E 6
Rh^{5+}	0.082	0.179	0.678	→	0.55_6	E 6
Ru^{3+}	0.250	0.237	0.736	→	0.68_6	E 6
Ru^{4+}	0.173	0.213	0.712	→	0.620_6	E 6
Ru^{5+}	0.101	0.202	0.701	→	0.565_6	E 6
Ru^{7+}	0.066	0.206	0.705	→	0.38_4	E 4
Ru^{8+}	0.042	0.229	0.728	→	0.36_4	E 4
S^{2-}	1.772	1.722	1.273	→	1.84_6	E 6
S^{4+}	−0.076	−0.075	0.424	0.426_6	0.37_6	D (14) m
S^{6+}	−0.241	−0.189	0.310	→	0.12_4	E 4
Sb^{3+}	0.354	0.351	0.850	→	0.76_6	E 6
Sb^{5+}	0.147	0.257	0.756	→	0.60_6	E 6
Sc^{3+}	0.326	0.321	0.820	0.738_6	0.745_6	D (16) b
Se^{2-}	1.912	1.912	1.413	→	1.98_6	E 6
Se^{4+}	0.017	0.035	0.534	→	0.50_6	E 6
Se^{6+}	−0.052	0.026	0.525	→	0.28_4	E 4
Si^{4+}	−0.078	−0.076	0.423	0.258_4	0.26_4	D (11) q
Sm^{2+}	0.788	0.761	1.260	1.206_8	1.27_8	D (11) n
Sm^{3+}	0.610	0.633	1.132	1.066_8	1.079_8	E 6
Sn^{2+}	0.819	0.781	1.280	→	1.22_8	E 8
Sn^{4+}	0.264	0.318	0.817	0.690_6	0.690_6	D (11) r
Sr^{2+}	0.899	0.878	1.377	1.282_8	1.26_8	D (11) n
Ta^{2+}	0.428	0.380	0.879	0.816_6	—	D (11) n
Ta^{3+}	0.302	0.294	0.793	→	0.72_6	E 6
Ta^{4+}	0.250	0.302	0.801	→	0.68_6	E 6
Ta^{5+}	0.130	0.305	0.804	0.631_6	0.64_6	E 8
Tb^{3+}	0.565	0.584	1.083	1.036_8	1.040_8	E 6
Tb^{4+}	0.339	0.444	0.943	0.774_6	0.76_6	D (11) f
Tc^{4+}	0.205	0.250	0.749	→	0.645_6	E 6
Tc^{5+}	0.147	0.257	0.756	→	0.60_6	E 6
Tc^{7+}	0.054	0.191	0.692	→	0.37_4	E 4
Te^{2-}	2.142	2.142	1.643	→	2.21_6	E 6

TABLE I—*Continued*

Ion[a]	First approach	Second approach				
	r_0	r_0	ρ_0	r_k[b]	$r_{k,S}$	Remarks[c]
Te^{4+}	0.626	0.734	1.233	→	0.97_6	E 6
Te^{6+}	0.095	0.277	0.776	→	0.56_6	E 6
Th^{4+}	0.575	0.737	1.236	1.089_9	1.09_9	D (11) f
Ti^{2+}	0.483	0.440	0.939	→	0.86_6	E 6
Ti^{3+}	0.234	0.220	0.719	0.667_6	0.670_6	D (11) k
Ti^{4+}	0.140	0.176	0.675	0.594_6	0.605_6	D (11) r
Tl^{1+}	1.312	1.292	1.791	1.570_8	1.59_8	E 6
Tl^{3+}	0.516	0.529	1.028	0.766_4	0.754_4	E 6
Tm^{2+}	0.703	0.672	1.171	→	1.03_6	E 6
Tm^{3+}	0.512	0.525	1.024	0.882_6	0.880_6	D (16) b
U^{2+}	0.744	0.715	1.214	1.061_6	—	D (11) n
U^{3+}	0.697	0.729	1.228	→	1.025_6	E 6
U^{4+}	0.494	0.635	1.135	0.992_8	1.00_8	D (11) f
U^{5+}	0.370	0.585	1.084	0.810_6	0.76_6	E 7
U^{6+}	0.315	0.548	1.047	→	0.73_6	E 6
V^{2+}	0.393	0.344	0.843	→	0.79_6	E 6
V^{3+}	0.185	0.166	0.665	0.630_6	0.640_6	D (11) k
V^{4+}	0.096	0.126	0.625	0.561_6	0.58_6	D (11) r
V^{5+}	−0.009	0.047	0.546	0.326_4	0.355_4	D (22)
W^{4+}	0.224	0.273	0.772	→	0.66_6	E 6
W^{5+}	0.173	0.288	0.787	→	0.62_6	E 6
W^{6+}	0.065	0.214	0.713	0.419_4	0.42_4	D (23)
Xe^{8+}	−0.009	0.327	0.826	0.429_4	0.40_4	E 6
Y^{2+}	0.705	0.674	1.173	1.031_6	—	D (11) n
Y^{3+}	0.523	0.538	1.037	0.890_6	0.900_6	D (17) b
Yb^{2+}	0.690	0.659	1.158	1.141_8	1.14_8	E 6
Yb^{3+}	0.502	0.512	1.011	0.872_6	0.868_6	D (17) b
Zn^{2+}	0.328	0.297	0.796	0.755_6	0.74_6	D (24)
Zr^{2+}	0.550	0.510	1.009	0.911_6	—	D (11) n
Zr^{4+}	0.245	0.328	0.827	0.697_6	0.72_6	D (11) f

Note. All radii in Ångstrom.

[a] HS and LS means high spin and low spin, respectively.

[b] Lower index after r_k or $r_{k,S}$ value indicates the coordination. Arrow means that r_0 was estimated from $r_{k,S}$ given in the next column; therefore r_k is the same as $r_{k,S}$.

[c] D means that r_0 was determined using all requirements of the assumed standard state. It is followed by a reference to the souce of the structural data and by a letter indicating the type of structure; b—bixbyite, c—cuprite, f—flourite or autifluorite, k—corundum, m—molecule, n—NaCl type, q—quartz, r—rutile. E means that r_0 was estimated from $r_{k,S}$; it is followed by a number k corresponding to $r_{k,S}$ used.

ciprocal of the bond length (reduced by certain value and thus converted into effective bond length) which is exactly to be expected in view of the linear E–s relation (cf. Ref. (*7*) and Eq. (7)). This leads also to a new model of chemical bonding in crystals which will be discussed below.

(*III*) *Numerical Data*

In view of the comment made at the end

of the Introduction simple oxides (Li_2O, Na_2O . . . MgO, CaO . . . Al_2O_3 . . . VO_2 . . . V_2O_5, etc.) at room temperature and at normal pressure were chosen as standard state for the respective ions. In the case of polymorphism the most stable form was usually used. Sometimes there are doubts, however, as to which polymorph is the most stable. On the other hand the crystallographic data are usually more precise for crystals of the highest symmetry, which are not necessarily the most stable. Therefore the choice of polymorph was sometimes done arbitrarily and the source of structural data was given in each case. It has been assumed that in the standard structures Eq. (2) is exactly fulfilled. Thus r_0 for each considered cation was determined by resolving Eq. (2) combined with Eq. (21) and by using the values of all bond lengths around cation in its standard structure. If the structure contained the cations in nonequivalent positions, all of them were of course taken into account. The fitted r_0 parameters are listed in Table I.

The procedure described above (including the choice of standard state and the way of calculations) could be used for about 35% of the considered ions marked with the letter D (= determined) in the last column of Table I. Due to various reasons, as, e.g., the lack of precise structural data or doubts concerning stoichiometry, r_0 values for the remaining ions were estimated using Eq. (14) and the most reliable $r_{k,\mathrm{S}}$ determined by Shannon. The latter procedure is justified by the fact that $r_{k,\mathrm{S}}$ and r_k from Eq. (14) are practically the same (cf. Fig. 3 and the respective comment in the text). Ions for which r_0 was estimated are marked in the last column of Table I with the letter E (= estimated) followed by number k corresponding to $r_{k,\mathrm{S}}$ used. The r_0' values for O^{2-} and F^{1-} result from Eqs. (11) and (12), respectively. As for other anions their r_0' values were estimated by using Eq. (11) and a = 0.0114 (an average of a for O^{2-} and F^{1-}). For the reader's convenience all parameters useful in r_k–k and s–R calculations are summarized in Table II. The proposed way of calculations is so simple that Table I may be easily and systematically completed and corrected by using the emerging structural data.

We propose to call r_0 values listed in Table I as *standard radii of free ions* and r_k values obtained from r_0 with Eq. (14) *standard ionic radii at coordination k.*

It seems useful to mention here that Table I also contains r_0 values resulting from the second approach at s–R relationship. They are obtained with an analogous procedure, using Eqs. (34) and (35) instead of (21) and Eq. (36) instead of (14). For easy comparison of the present and the earlier data r_k calculated from r_0 and $r_{k,\mathrm{S}}$ are also included into Table I. To limit the size of Table I comparison of r_k and $r_{k,\mathrm{S}}$ was done only in terms of the second approach which is considered as the final one. But, r_k are nearly the same in both approaches and close to $r_{k,\mathrm{S}}$.

TABLE II

PARAMETERS FOR r_k–k AND s–R CALCULATIONS

Parameter	First approach	Second approach
a_0 or d_0	$a_0 = 0.0811$	$d_0 = A - Bz$ $= 0.1177 - 0.0081\,z$
b	0.0379	$b = C + \mathrm{D}z$ $= 0.0347 + 0.0050\,z$
$r_0'(O^{2-})$	1.328	1.328
$a_0'(O^{2-})$	0.0118	0.0118
$r_0'(F^{1-})$	1.265	1.265
$a_0'(F^{1-})$	0.0110	0.0110
a_0' assumed for other anions	0.0114	0.0114
$h = -r_0(H^{1+})$	0.493	0.499

Electrostatic Hover Model of Crystal Structure

From Eqs. (17), (20), and (21) we see that bond strength is proportional to the reciprocal of the bond length[2] reduced by $R_0 = r_0 + r_0'$. The difference

$$L = R - R_0 \tag{22}$$

may be considered as the effective bond length. On the one hand, this result is consistent with the linear relation between bond strength and bond energy suggested in (7), namely:

$$E \sim s \sim \frac{\text{const}}{L}. \tag{23}$$

On the other hand, this leads to a new model of crystal structure which may be called as *an electrostatic hover model* (cf. Fig. 4). In this model ions are of constant size (r_0 and r_0'). They do not touch but they are fixed in the space at distances L with electrostatic forces. The ions behave as if an effective charge was localized at both ends of L. This charge may be considered as excess negative charge of anion and an electron hole on cation, both localized on orbitals and not at the centers of the ions as usually assumed.

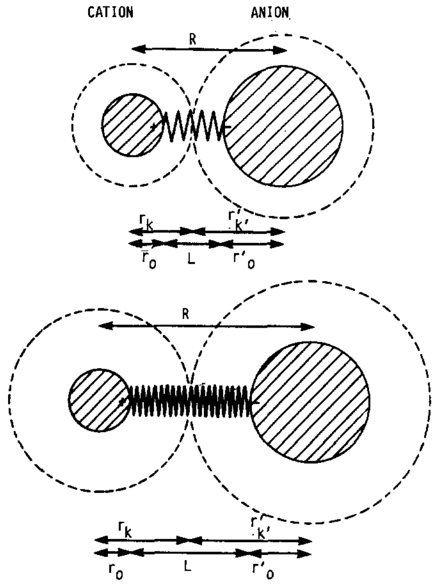

FIG. 4. Comparison of the electrostatic hover model of crystal structure with traditional model of close packing (details are discussed in text).

The effective bond length L is marked simplistically in Fig. 4 as a spring. The shorter L, the stronger the bond; the longer L the weaker the bond. In this model r_k values lose their physical sense. It is rather L_k that should be correlated with k. But mathematically r_k values may still be used to determine L at given coordination or at given bond strength. As results from Fig. 3 and Eqs. (10) and (11) the most typical values of $L_k = ak + a'k'$ vary between 0.3 and 0.5 Å.

The positions of ions in the space must result from the equilibrium between attractive and repulsive forces. The latter may be thought to result from the interactions between the ions of the same charge. This problem shall require further, more thorough considerations.

Obviously one can still consider a crystal as built of close-packed ions of radii r_k and $r'_{k'}$. But, if so, one is forced to accept that (with the exception of some highly symmetrical structures) ions are no longer spherical, but their size depends on the angle and varies (adapts) on passing from one structure to the other ("barbapapa behavior"). An example is given in Fig. 5a where the shape of a cation resembles a deformed rugby ball. If we change the configuration of the same ions, the cation is further deformed (Fig. 5b). One has also to accept

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[2] It should be stressed that although a coulombic-type s–R relationship was expected by the author before undertaking the present studies, the shape of Eqs. (17), (20), (21), and (23) is not influenced by that preliminary supposition, but it is a logical consequence of the observed r_k–k dependence expressed by Eqs. (10) and (14).

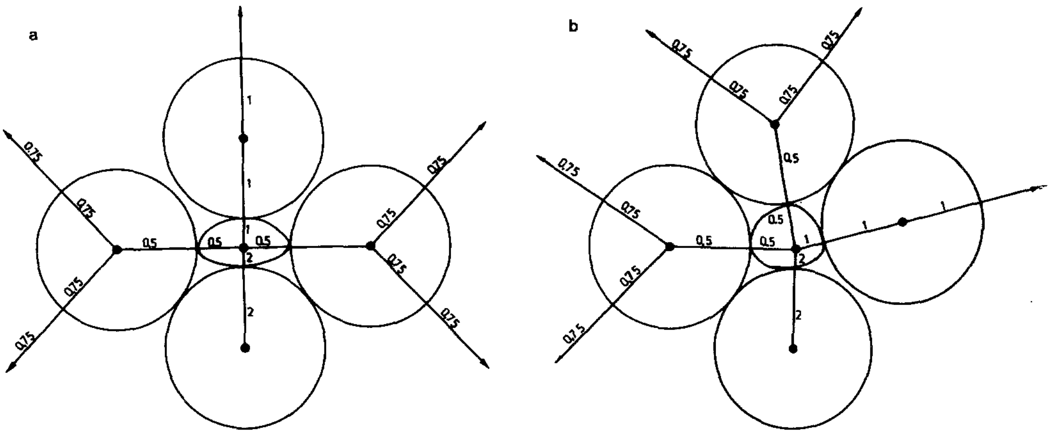

FIG. 5. Examples of close-packed structure in which ions adapt their size and shape to the strength of bonding (indicated by numbers). Central cation resembles a deformed rugby ball (a) or an irregular lens (b). Very small deformations of anions (comparable with the width of line) are neglected. Figure is based on r_k, r'_k, and s for Ti^{4+}–O^{2-} bond.

that the weaker the bond, the larger the ion, but if the bond is entirely broken the ion becomes small again. The traditional description of crystal structure contains the premise that an increase of r_k with k is the intrinsic property of ions. But in terms of the electrostatic hover model, it is clear that with increasing k the binding ability of cation (valence, charge) is divided among increasing number of neighboring anions. Therefore each bond must become weaker and longer. It seems that the latter formulation is much more logical. Moreover, in terms of the electrostatic hover model the ions in a crystal have a space to vibrate and to diffuse. This was entirely forgotten when the model of close-packed ions was being formulated.

Second Approach to the *s*–*R* Relationship

As mentioned in the preceding paragraph r_k values lose their physical sense in terms of the electrostatic hover model of crystal structure. It is rather the effective bond length

$$L = ak + a'k' \qquad (24)$$

that should be correlated with coordination or bond strength. To take this fact into account we can repeat the calculations assuming that the ionic radius of oxygen anion is constant ($r'_0 = 1.328$) and ascribing formally $a'k'$ to the cation instead of the anion. We have now

$$r_k^* = r_k + a'k' = r_0 + ak + a'k' \qquad (25)$$

and in review of Eq. (15):

$$r_k^* = r_k + a'\frac{2k}{z} = r_0 + ak + a'\frac{2k}{z} \qquad (26)$$

or

$$r_k^* = r_0 + dk, \qquad (27)$$

where

$$d = a + \frac{2a'}{z}. \qquad (28)$$

Values of d and r_0 for the same 58 cations as considered in the first approach, were

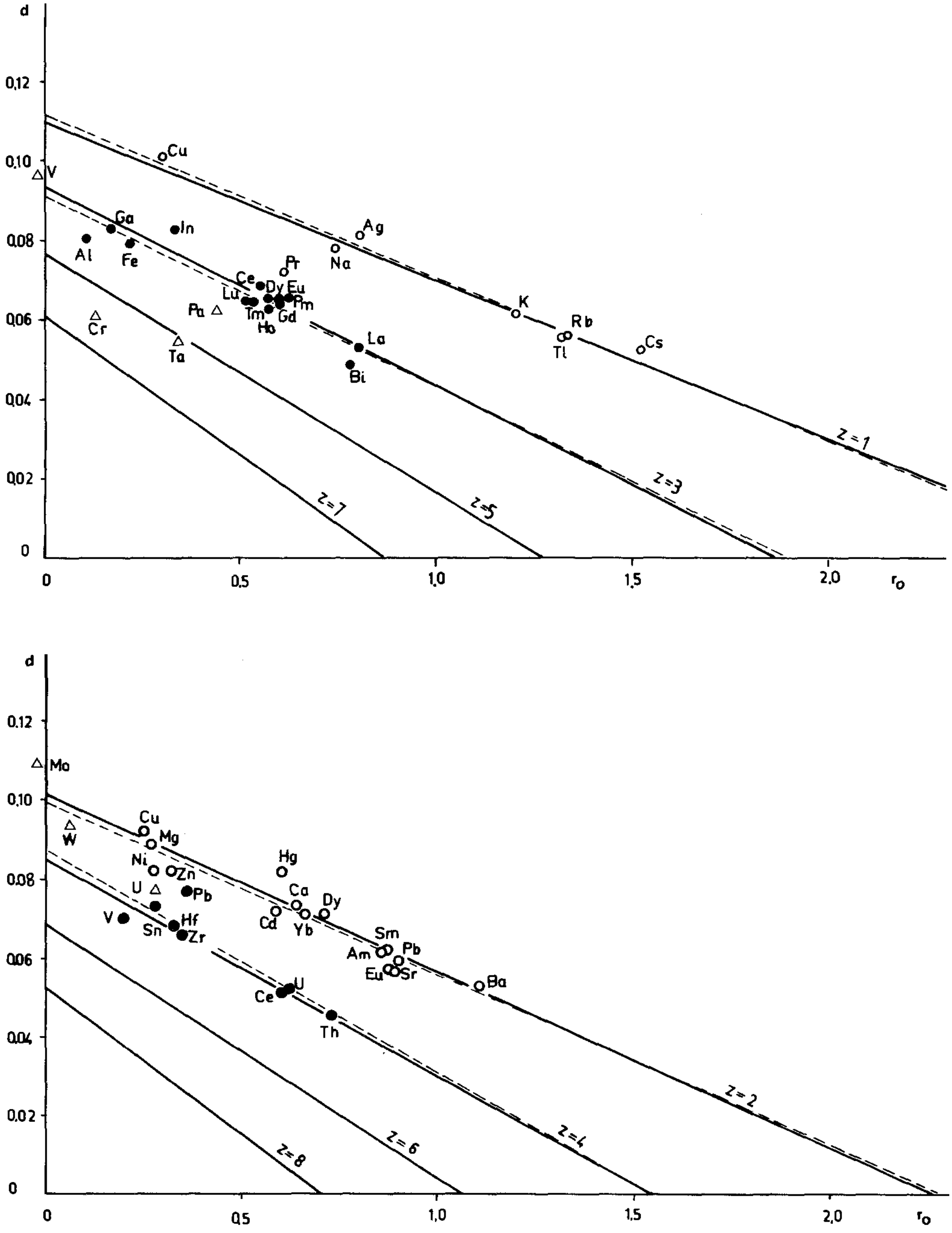

FIG. 6. Dependence between parameters d and r_0 from Eq. (27) for ions of various valences (second approach). Dotted lines are determined with the least-squares method. Solid lines are obtained after final smoothing (cf. text and Fig. 7). Due to overlapping the points for trivalent ions of Er, Sm, Tb, Y, and Yb (at about $r_0 = 0.55$, $d = 0.065$) are omitted. Triangles represent penta- and hexavalent ions.

determined with Eq. (27). As seen in Fig. 6 in analogy to Eq. (10), d is linearly related to r_0:

$$d = d_0 - br_0, \qquad (29)$$

but ions of z equal to 1, 2, 3, and 4 trace four different straight lines of d_0 and b dependent on z. The points fit much better the d–r_0 lines (Fig. 6) than a–r_0 lines (Fig. 3), the correlation coefficients being 0.988, 0.957, 0.950, and 0.917 for z changing from 1 to 4, respectively, while c was only 0.889 for the a–r_0 line. As for trivalent ions the large number of points is grouped at about $r_0 = 0.55$ and $d = 0.065$. To equalize the statistical weight they were replaced with one average point. Without it $c = 0.895$. The few points corresponding to penta- and hexavalent ions are irregularly dispersed. The dispersion may be ascribed to an inaccuracy in determination of their r_k, resulting, as already mentioned, from distortion of polyhedra in which these ions usually appear (*10*). It has been therefore assumed that d_0 and b should regularly depend on z. In Fig. 7, d–z relationship are drawn at six chosen r_0 values: 0, 0.25, 0.50, 0.75, 1.00, and 1.25. They are linear:

$$d = \alpha - \beta z. \qquad (30)$$

The parameters α and β at each chosen r_0 values were determined with the least-squares method and smoothed d values at the six above-mentioned r_0 levels were calculated with Eq. (3) for valences ranging from +1 to +8. On this basis smoothed d–r_0 lines (not illustrated) were again determined with the least-squares method. It was found that all eight smoothed d–r_0 lines cross one another at $r_0 = -1.63$ and $d = 0.174$ with accuracy better than 0.5%. This may be considered as the common point I. Distances between these lines at $r_0 = 1.00$ are exactly the same and equal to 0.0131, with $d = 0.0699$ for monovalent ions. At $r_0 = 1.00$ we have thus eight points II_z of the ordinates dependent on z. The final smoothing consisted in assuming that the d–r_0 lines for various z pass exactly through the above-indicated points I and II_z. This gives

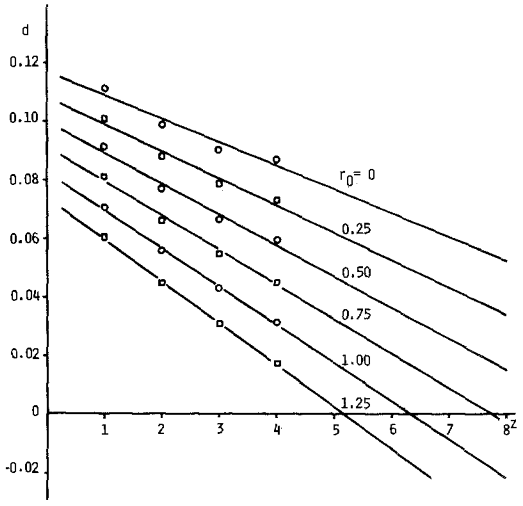

FIG. 7. Dependences of d on z at various r_0 (sections constructed on the basis of Fig. 6).

$$d_0 = A - Bz \qquad (31)$$

and

$$b = C + Dz \qquad (32)$$

with $A = 0.1177$, $B = 0.0081$, $C = 0.0347$, $D = 0.0050$ (cf. Table II). The final d–r_0 lines are shown in Fig. 6 (solid lines). The second approach presented above results in modification of the s–R relationship. Namely, in terms of this approach the bond length R may be expressed as

$$R = r_k^* + r_0'. \qquad (33)$$

Making use of Eqs. (27), (29), and (10) we arrive finally at

$$s = \frac{zd_0 - zbr_0}{R - r_0 - r_0'} = \frac{dz}{R - R_0}, \qquad (34)$$

where

$$d = 0.1177 - 0.0081z - 0.0347r_0 - 0.0050zr_0. \qquad (35)$$

In terms of the second approach the standard radii r_0 (listed in Table I and marked with D) were determined in a way analogous to the first approach, i.e., using the proposed standard state and Eqs. (34) and (35) instead of (21). For the remaining cations r_0 values were estimated (E) using the most reliable $r_{k,S}$ (indicated in Table I) and the equation

$$r_0 = r_k + \frac{2a'k}{z} - dk. \quad (36)$$

This equation is derived from Eqs. (26) and (27). The standard radii r'_0 for anions are the same as in the first approach.

Due to the better accuracy (cf. Figs. 3 and 6) and better rationalization in terms of the electrostatic hover model the second approach is thought to be preferable. Therefore the final conclusion of the discussion performed in this paper, concerning the *s–R–r–k* problem is thought to be expressed by Eqs. (27), (36), and (34) with values of r_0 and all other necessary parameters gathered in Tables I and II under "second approach."

Evaluation of the New Set of the Standard Ionic Radii. New Scale of the Absolute Ionic Radii

The effective ionic radii of Shannon (*10*) were determined according to the procedure which essentially consisted in taking an average of a given cation–anion bond lengths from a large number of structures, subtracting the assumed anion radius (r'_6 = 1.40 Å for O^{2-}) and adjusting the obtained cation radius to be consistent with plots of radii vs unit cell volume, radii vs coordination, radii vs oxidation state, and with empirical bond-length–bond-strength relationships.

The new set of the standard r_0 and r_k radii proposed in this paper results from: (i) the newly formulated linear $r_k - k$ dependence, (ii) the newly formulated *s–R* dependence (in both of them r_0 appears as parameter), and (iii) the normalization in terms of the proposed standard state.

As both ways of calculations are different, the effective ionic radii $r_{k,S}$ and the standard ionic radii r_k need not necessarily be the same though they should be similar. In fact for the majority of ions the differences between $r_{k,S}$ and r_k are smaller than 0.03 Å. There are only few exceptions (Ag^{1+}, Cs^{1+}, K^{1+}, Mn^{3+}HS, Mo^{6+}, Na^{1+}, Pb^{2+}, S^{4+}) where these differences exceed 0.05 Å. As shown in Fig. 8 the plots of r_0 vs oxidation state for ions of the noble gas shell follow the expected regular dependences. As it may be easily deduced from Table I also the plots of r_0 vs oxidation state for a given element are usually regular, r_0 diminishing with increasing z. Some ions (Fe^{4+}, Mn^{6+}, N^{3+}, Np^{6+}, Np^{7+}, Os^{6+}, Os^{7+}, Os^{8+}, Pa^{3+}, Pu^{6+}, Re^{7+}, Ru^{8+}, Ta^{4+}, Ta^{5+}, Tc^{5+}, U^{3+}, W^{5+}) lie slightly off regular curves, while the niobium ions form an entirely irrational set. As these are mostly rather exotic ions the discrepancies can be ascribed to an experimental error. The r_0 values for these ions should be rather read from the respective r_0–z curves by interpolation or extrapolation. As this procedure involves some arbitrariness, the author's intention is to leave this problem open.

It seems interesting to note that some of our standard ionic radii were determined by using structural data for molecules in which bonding is undoubtly covalent (though polarized). We may quote here C^{4+}, H^{1+}, S^{4+} for which r_k were found to be -0.078_3, -0.393_1, 0.424_6, and $r_{k,S}$ are -0.08_3, -0.38_1, and 0.37_6, respectively. Thus, in spite of this unusual way of determination of ionic radius, the agreement between r_k and $r_{k,S}$ is excellent for C^{4+} and H^{1+} and satisfactory for S^{4+}. This observation combined with the fact that the concept of the electrostatic bond strength can be also used for crystals with primarily covalent bonds (*3*) proves again that some aspects of ionic and covalent bonding are highly analogous.

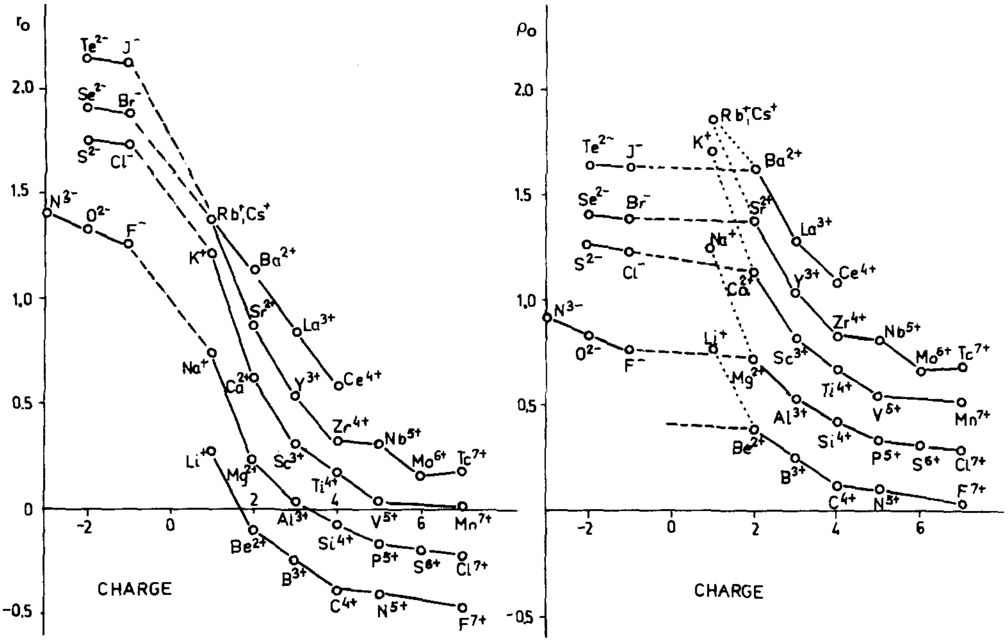

FIG. 8. Standard radii r_0 and absolute radii ρ_0 of some ions of the noble gas shell as function of the oxidation state.

There are 20 ions for which standard r_0 radii were found to be negative. The problem of the negative ionic radii has already been discussed in detail by Shannon and Prewitt (*9*) who also found the negative values for H^{1+} ($k = 1$), C^{4+} ($k = 3$), and N^{5+} ($k = 3$). These authors note that there is intrinsically no objection to the negative radii as the cations may be thought to penetrate the electronic cloud of a highly deformed oxygen ion. It seems that this concept could be acceptable for H^{1+} at $k = 1$. But negative radii for C^{4+} and N^{5+} at $k = 3$ would force us to accept that electronic clouds of three adjacent anions are strongly overlapped. The more so a physical sense can be hardly attributed to the negative r_0 radii of so heavy and complex ions as, e.g., Fe^{6+} or Mn^{6+}. There are also numerous ions for which r_0 or $r_{k,S}$ was found to be positive but irrationally small. The alternative way to resolve this problem could consist in ascribing much smaller values to anionic radii (*9*). In fact there is no unequivocal manner of dividing a bond length among anion and cation and thus the question of absolute radii is still not resolved.

In view of the present work the following solution may be suggested. The r_0 value for H^{1+} (i.e., for a proton) was found to be

$$r_0(H^{1+}) = -h = -0.499 \text{ Å}. \quad (37)$$

The absolute size of proton is of the order of 10^{-5} Å, i.e., much smaller than the accuracy of the determination of ionic radii. Thus it seems natural to take the absolute radius, ρ_0, of H^+ as 0.00. Consequently ρ_0 for all cations may be suggested to be

$$\rho_0 = r_0 + 0.499 \quad (38)$$

and for anions

$$\rho_0' = r_0' - 0.499. \quad (39)$$

In particular, for oxygen anion ρ_0 is 0.829.

Taking into account that nonpolar covalent radius of oxygen has been estimated to be 0.73 (*25*) and that O^{2-} formation ($O + 2e = O^{2-}$) consists in location of two electrons on the same shell which is already partly occupied in oxygen atom, the above indicated value of ρ_0' seems to be quite reasonable. For convenience ρ_0 and ρ_0' values are also listed in Table I.

Assuming this new scale of *the absolute ionic radii* results in having positive radii for all the ions of all the elements (with exception of N^{3+}, which may be ascribed to an experimental error). Simultaneously the ρ_0–z plots for isoelectronic ions of noble gas shell (Fig. 8) become more flat which seems to be reasonable as an increase of nucleus charge at the same electronic shell should not result in so strong sigmoid jump between monovalent anions and low-valent cations as observed in the r_0–z plots.[3] There is only one discrepancy consisting in the fact that ρ_0 values for monovalent cations as Na^{1+}, K^{1+}, Rb^{1+}, and Cs^{1+} are larger than those for F^{1-}, Cl^{1-}, Br^{1-}, and I^{1-}, respectively. An explanation of this phenomenon cannot be offered at present.

It seems useful to note that in view of Eqs. (18), (35), (38), and (39):

$$R_0 = r_0 + r_0' = \rho_0 + \rho_0' = P_0 \qquad (40)$$

and

$$d = 0.1177 - 0.0081z - 0.0347\,(\rho_0 - h) - 0.0050z(\rho_0 - h) = 0.1350 - 0.0056z - 0.0347\,\rho_0 - 0.0050z\rho_0. \qquad (41)$$

Thus Eq. (34) may be transformed to

$$s = \frac{dz}{R - P_0} \qquad (42)$$

with d expressed by Eq. (41). As is evident, bond strength calculated with Eq. (34) or (42) is numerically the same.

If useful, also ρ_k may be defined by combining Eqs. (36) and (38) as

$$\rho_k = \rho_0 - \frac{2a'k}{z} + dk. \qquad (43)$$

Evaluation of the Bond Strength Data

Introduction of the standard state for bond strength results in a number of consequences. First of all, the bond strength sums around cations in simple oxides at standard state are—from definition—exactly equal to the nominal cation valences. However, if the structure of a simple oxide contains m cations in crystallographically nonequivalent positions, the bond strength sum around all of them amounts to mz, while Σs around each of them is not necessarily equal to z. This means that nonequivalent cations (as well as nonequivalent anions) are not necessarily bonded with the same strength (energy), though the expected Σs should not be very different from z (conclusion I). This is analogous to organic and inorganic molecules where the heat of dissociation of C–O, C–H, or O–H bonds varies on passing from the molecule of one compound to another. The more so, the bond strength sums around cations and anions in various complex oxides or oxysalts may, and even should be differentiated. As for the thermodynamically stable crystals the bond strength sums $(\Sigma s)_{cat}$ around all chemically and crystallographically nonequivalent cations should be higher than $(\Sigma s)_{cat}^{ox}$ expressing the analogous sums in simple oxides taken in an equivalent number. In other words, in view of the assumed standard state, they should be higher than the respective sums of the nom-

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[3] Besides the ionic radii determined from crystal structures ($r_{k,S}$, r_k, r_0, ρ_0) the "atomic radii" r_a are known (*26*) as they are obtained from quantum-chemical computations (in fact these are also "ionic radii" determined for various z). The r_a–z plots for low-valent cations of noble gas shell are yet more flat than ρ_0–z plots. This may be ascribed to the fact that r_a concern the ions of charge z while the effective charge of cations in crystal lattices is always smaller than their formal valence z.

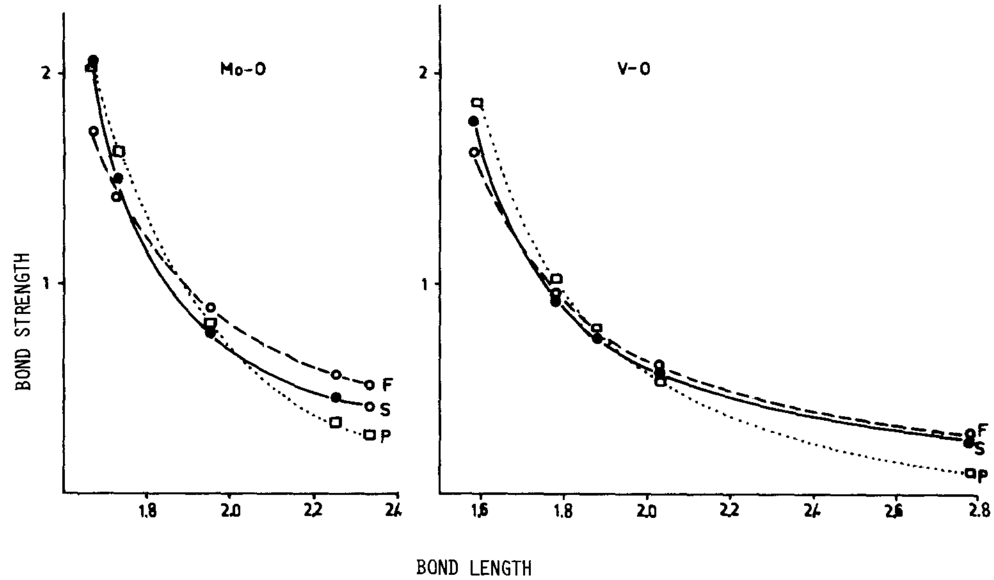

FIG. 9. Bond strength of Mo–O and V–O bonds in MoO_3 and V_2O_5 calculated from power-type equation (P); coulombic-type equation, first approach (F), and coulombic-type equation, second approach (S) (Eqs. (4), (21), and (34), respectively).

inal valences of cations (conclusion II).[4]

In view of the above comments and the brief outline of the bond-strength concepts given in the Introduction it is impossible to decide quantitatively whether s values calculated with Eq. (34) are better or worse than those resulting from Eqs. (4), (5), or (21). One can say, however that both Eq. (21) and (34) are logical consequences of the well argued linear r_k–k and a–r_0 or d–r_0 relationships and that—as far as possible—they are rationalized in terms of the electrostatic hover model of crystal structure. Due to both of them the values of ionic radii and the parameters for calculating cation–oxygen bond strength have been made consistent. The linear relationships for Eq. (34) are more accurate than those leading to Eq. (21). Another important argument (E–s–R relationship) will be offered in a forthcoming paper (*8*). These facts speak in favor of Eq. (34), which seems to be conceptually better.

It seems of interest to verify the above-mentioned conclusions I and II. The respective examples are shown in Fig. 9 and in Tables III and IV. Figure 9 shows the bond strength values for Mo–O and V–O bonds in MoO_3 and V_2O_5 resulting from the power-type equation (P, Eq. (4)), and from the equations of the first (F, Eq. (21)) and the second (S, Eq. (34)) approaches. In Table III, Σs values around cations and anions in MoO_3, V_2O_5, and in several oxysalts are compared. Table IV contains the bond strength sums $(\Sigma s)_{\text{cat}}$ around all nonequivalent cations in a number of structures compared with $(\Sigma s)_{\text{cat}}^{\text{ox}}$ expressing, as already mentioned, the analogous sums in simple oxides taken in an equivalent quantity. As seen from Fig. 9 and Table III the values of

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[4] Exactly speaking, this is the bond energy sum (around all nonequivalent cations) which should be higher than the analogous sum in simple oxides. If Eq. (7) was valid and coefficients J for various cation–oxygen bonds were differentiated, conclusion II would have only an approximate character. The problem will be undertaken again in the forthcoming paper (*8*).

TABLE III

BOND STRENGTH SUMS AROUND CATIONS AND ANIONS IN SOME CRYSTALLINE STRUCTURES[a]

	MgV_2O_6			CuV_2O_6			CdV_2O_6		
	P	F	S	P	F	S	P	F	S
Me^{2+}	1.86	1.92	1.92	2.02	2.14	2.18	2.17	2.39	2.34
V^{5+}	5.10	4.93	4.87	5.12	4.94	4.88	4.99	4.86	4.77
O_1	1.95	1.77	1.81	1.97	1.83	1.90	2.03	1.91	1.93
O_2	1.96	1.96	1.96	2.01	2.00	1.98	1.99	2.02	1.99
O_3	2.11	2.16	2.06	2.15	2.18	2.09	2.06	2.12	2.02

	V_2O_5			MoO_3		
	P	F	S	P	F	S
V^{5+}/Mo^{6+}	5.11	5.00[b]	5.00[b]	5.92	6.00[b]	6.00[b]
O_1	1.96	1.91	2.03	2.04	1.72	2.06
O_2	2.06	1.87	1.83	1.98	1.99	1.96
O_3	2.11	2.15	2.05	1.90	2.28	1.98

[a] P—from power-type function (Eq. (4)), F—from coulombic-type function, first approach (Eq. (21)), S—from coulombic-type function, second approach (Eq. (34)). Structural data for MgV_2O_6, CuV_2O_6, CdV_2O_6, V_2O_5, and MoO_3 taken from (27), (28), (29), (22), and (20), respectively.

[b] From definition.

s and Σs around cations and anions resulting from P, F, and S versions are only slightly differentiated and Σs are close to z or z', respectively. This remains in agreement with conclusion I. This is not so with conclusion II. As seen from Table IV the differences $\Delta = (\Sigma s)_{cat} - (\Sigma s)^{ox}_{cat}$ which should be positive are in fact (in both S and

TABLE IV

BOND STRENGTH SUMS $(\Sigma s)_{cat}$ AROUND ALL NONEQUIVALENT CATIONS IN SOME OXIDE STRUCTURES COMPARED WITH ANALOGOUS SUMS $(\Sigma s)^{ox}_{cat}$ IN SIMPLE OXIDES

Compound	S			P			Source of structure data
	$(\Sigma s)_{cat}$	$(\Sigma s)^{ox}_{cat}$	Δ	$(\Sigma s)_{cat}$	$(\Sigma s)^{ox}_{cat}$	Δ	
$MgAl_2O_4$	7.84	8.00	−0.16	7.87	8.10	−0.23	*(11)*
$ZnAl_2O_4$	8.02	8.00	+0.02	7.96	8.02	−0.06	*(11)*
$CoAl_2O_4$	8.04	8.00	+0.04	7.85	7.98	−0.13	*(11)*
$FeAl_2O_4$	7.78	8.00	−0.22	8.06	8.20	−0.14	*(11)*
$MgCr_2O_4$	7.93	8.00	−0.07	7.47	7.74	−0.27	*(11)*
MgV_2O_6	11.66	12.00	−0.34	12.06	12.18	−0.12	*(27)*
CdV_2O_6	11.88	12.00	−0.12	12.15	11.98	+0.17	*(28)*
CuV_2O_6	11.94	12.00	−0.06	12.26	12.29	−0.03	*(29)*
$CuWO_4$	7.90	8.00	−0.10	8.01	8.41	−0.40	*(30)*
$CoMoO_4$	7.89	8.00	−0.11	7.80	7.76	+0.04	*(31)*
$CuMoO_4$	7.51	8.00	−0.49	8.18	7.99	+0.17	*(32)*

Note. $\Delta = (\Sigma s)_{cat} - (\Sigma s)^{ox}_{cat}$, S—from Eq. (34) of the second approach, P—from power-type Eq. (4).

P versions) sometimes positive and sometimes (more frequently) negative. This disagreement may result to some extent from inaccuracy of the structural data. Let us mention that an error of 0.01 Å in the length of very short V–O or Mo–O bond may result in changing s by 0.05 to 0.1 vu (cf. Fig. 9). On the other hand, s values for, e.g., $MgAl_2O_4$ were calculated using $u = 0.387$ (the crystallographic parameter u indicates the positions of oxygen in spinel structure). It may be easily verified that if $u \leq 0.381$ or $u \geq 0.396$ Δ would be positive. The latter value remains within the limit of error of the older determination (33) where u was found to be 0.390 ± 0.006. However, at $u = 0.396$ the bond strength sums around cations are rather far from their z (1.50 and 3.26 for Mg^{2+} and Al^{3+}, respectively).

The above considerations cannot cover the fact that the s–R dependences of P, F, and S type are still empirical equations and thus their precision depends on the used empirical data and on simplifications introduced in the mathematical procedure (e.g., linear relationships). Therefore numerical coefficients in Eq. (34) proposed in this paper shall probably require further refinement. Some new experimental data would be highly desirable, especially those necessary to draw d–r_0 lines for high-valent cations and to verify our smoothing procedure.

Conclusions

The main findings of this paper are gathered in the Abstract. The main aim of the paper was to construct the system of equations linking logically the values of bond strength, bond length, ionic radii, and coordination number. With these equations the numerical values of s and r_0 or r_k form mutually consistent sets which may find application in the analysis of crystal structures. The quality of the present numerical data is approximately the same as of those previously published, but new meaning is ascribed to the bond strength concept due to the defined standard state. As far as possible the established relationships are rationalized in terms of the introduced electrostatic hover model of crystal structure. A new ρ-scale of the absolute ionic radii is proposed which seems to be more rational than the former. The striking conclusion is that also some properties of covalent bonds may be interpreted as if they were ionic.

There remain some inconsistencies in the picture outlined above which have been indicated in the last two sections. This should inspire further, more profound studies.

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