

## Empirical Relationship between Individual Cation-Oxygen Bond Length and Bond Energy in Crystals and in Molecules

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A new relation linking the length  $R$ , the strength  $s$ , and the atomization energy  $E$  of the individual bond in oxide crystals is postulated and discussed. The same function seems to be applicable to oxygen-containing molecules. The proposed equation is

$$E = Js = J \frac{dz}{R - R_0} = \frac{E_a^0}{m} \frac{d}{R - R_0} \text{ [kcal mole}^{-1}\text{]}$$

where coefficient  $J$  is equal to the standard atomization energy  $E_a^0$  of the simple oxide of the considered cation divided by the number  $m$  of cations in the formal molecule and by cation valence  $z$  (e.g., for Al-O bonds  $\text{Al}_2\text{O}_3$  is to be taken with  $m = 2$  and  $z = 3$ ). As already discussed previously (J. Ziółkowski, *J. Solid State Chem.* 57, 269 (1985)),  $d = 0.1177 - 0.0081z - 0.0347r_0 - 0.0050zr_0$  and  $R_0 = r_0 + r'_0$ , where  $r_0$  and  $r'_0 = 1.328 \text{ \AA}$  are the standard radii of free cation and oxygen anion, respectively. The  $r_0$  values for over 200 cations were determined and listed in the paper quoted above. In view of the above-indicated relationship between  $E$  and  $R$ , bond strength, being a somewhat artificial quantity, is no longer necessary. Possibilities and limitations of the applicability of  $s$  and  $E$  in the analysis of crystal structures are discussed in detail. © 1985 Academic Press, Inc.

### Introduction: Outline of the Concept

The molar atomization energy of an oxide crystal  $M_m\text{O}_n$  may be expressed as

$$E_a = -\Delta H_f + mS + \frac{n}{2}D, \quad (1)$$

where  $-\Delta H_f$ ,  $S$ , and  $D$  are: heat of formation of  $M_m\text{O}_n$ , heat of metal sublimation (or more generally heat of atomization of  $M$ ), and heat of dissociation of  $\text{O}_2$  molecule, respectively. If all heats are considered at standard state (normal pressure, 298 K) Eq.

(1) gives the standard value of  $E_a^0$ . If we deal with a crystal in which all cation-anion distances are of equal length, atomization energy of the individual bond (denoted further as bond energy) may be easily calculated as

$$e = \frac{E_a}{mNk}, \quad (2)$$

where  $N$  is the Avogadro's constant and  $k$  is the coordination number of cation. Consequently the bond energy per 1 mole of the equivalent bonds is

$$E = Ne = \frac{E_a}{mk}. \quad (3)$$

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However, in the majority of crystals the cation-anion distances are differentiated in length and certainly in energy so that

$$E_a = \sum_1^{mk} E_i = N \sum_1^{mk} e_i, \quad (4)$$

where  $mk$  involves all nonequivalent bonds around cations.<sup>1</sup> As the individual bond energies  $E_i(e_i)$  are experimentally inaccessible Eq. (4) remains useless and employing Eqs. (2) and (3) one can only calculate an average  $\bar{e}$  or  $\bar{E}$ .

The present paper aims at finding an empirical relation between the individual bond length and the individual bond energy in oxide crystals with use of the electrostatic bond strength as a quantity linking both of them.

As reviewed by Brown (1), several empirical methods for calculating cation-oxygen bond strength as function of bond length have been proposed so far, two of them becoming widely applicable and accepted. These are the inverse power function

$$s = \left(\frac{R}{R_1}\right)^{-N} \quad (5)$$

and the exponential function

$$s = \exp[(R - R_1)/B], \quad (6)$$

where  $s$ —bond strength in valence units (vu),  $R$ —bond length in Å,  $R_1$ ,  $N$ , and  $B$ —empirical parameters determined and listed in (1-4). The above functions have, however, no precise physical sense.

Recently (5) one of us has proposed for the same purpose the coulombic-type equation

$$s = \frac{dz}{R - R_0}, \quad (7)$$

where  $z$  is the valence of cation

<sup>1</sup> If the number of crystallographically nonequivalent cations is higher than  $m$  Eq. (4) should be expressed in the respective, more general form.

$$d = 0.1177 - 0.0081z - 0.0347r_0 - 0.0050zr_0 \quad (8)$$

$$R_0 = r_0 + r'_0 \quad (9)$$

$r_0$  and  $r'_0 = 1.328$  Å are the standard radii of free cation and oxygen anion, respectively (as explained below).

Let us recall, that as shown in (5), cationic radii  $r_k$  (6) are linearly dependent on coordination number  $k$ :

$$r_k = r_0 + dk - \frac{2a'k}{z}, \quad (10)$$

where  $a' = 0.0118$ ,  $d$  is defined as above (Eq. (8)), and  $r_0$  is the extrapolated radius of the free cation. Let us note that in both Eqs. (7) and (10) beside general parameters there appears only one specific parameter  $r_0$  reflecting the individuality of the cation forming a bond with oxygen. In the preceding paper (5) the necessity to choose a standard state for ionic radii and for bond strength has been pointed out and argued. Structures of simple oxides at room temperature and at normal pressure were chosen as the standard state for the respective ions, in which the sum of the strengths of bonds around the cation has been assumed to be exactly equal to  $z$ . At the so defined standard state, the standard  $r_0$  radii of the free ions for numerous ions were determined and listed in (5).

It also seems worth recalling that the shape of Eq. (7) may be rationalized in terms of the *electrostatic hover model* of crystal structure (5). In this model ions are considered to be of constant size ( $r_0$ ,  $r'_0$ ), they do not touch one another, but they are fixed in the space at distances  $L = R - R_0$  with electrostatic forces. The cations and anions behave thus as if an effective charge was localized at both ends of  $L$  rather than in their centers, as traditionally assumed. If so, we have

$$s \sim \frac{\text{const}}{L} \quad (11)$$

which means that  $s$  may be considered as a coulombic bond energy divided by a number, constant for a given cation. Consequently we may surmise<sup>2</sup> that

$$E = Js \quad (12)$$

and in view of Eq. (4):

$$E_a = J \sum_1^{mk} s_i, \quad (13)$$

where  $E$  and  $E_a$  are intended to be expressed in kcal mole<sup>-1</sup>,  $s$  in vu, and  $J$  in kcal mole<sup>-1</sup> vu<sup>-1</sup>. At the standard state we have  $E_a = E_a^0$  and  $\sum s_i = mz$ , thus, as results from Eq. (13):

$$J = \frac{E_a^0}{mz}. \quad (14)$$

Finally, by combining Eqs. (7), (12), and (14) the individual bond-length-bond-energy relation may be expressed as

$$E = J \frac{dz}{R - R_0} \quad (15)$$

or

$$E = \frac{E_a^0}{m} \frac{d}{R - R_0}, \quad (16)$$

$s$  being no longer necessary.

Equation (12) and its modifications (13), (15), (16), although argued, have a hypothetical character and obviously require an experimental verification. The attempt undertaken in this paper is based on the following concept. On heating the crystal at normal pressure from room temperature (standard state) to a given temperature  $T$  its  $E_a$  decreases as

$$E_a(T) = E_a^0 - \int_{298}^T C_p dT, \quad (17)$$

where  $C_p$  is the heat capacity. For many crystals  $E_a(T)$  can be easily calculated using known thermochemical data. On the other

<sup>2</sup> Equation (12) has been suggested for the first time in (7).

hand, a crystal dilates on heating, the bonds becoming longer and longer. Bond lengths as a function of temperature can be determined with X-ray analysis. Knowing them one can calculate bond strengths (Eq. (7)), construct the  $E_a(T)$  vs  $\sum_1^{mk} s_i$  dependence (denoted briefly as  $E-s$ ) and finally verify the validity of Eqs. (12)–(16).

Generally, the relative temperature changes in length of various bonds in crystals of a low point symmetry are not the same (anisotropy of thermal expansion). To learn them, the structure of a crystal should be entirely resolved at various temperatures. On the other hand, in some highly symmetrical structures the lengths of all bonds are equal and directly related to the lattice parameter. So it is, e.g., for MgO, CdO, and NiO crystallizing in the cubic NaCl type where  $R$  equals simply half of the lattice parameter  $a$ . We shall profit by it in this work. Two other crystals of lower symmetry will be also considered: tetragonal TiO<sub>2</sub>-rutile and hexagonal Al<sub>2</sub>O<sub>3</sub>-corundum. In both of them metal atoms are octahedrally coordinated, TiO<sub>6</sub> octahedra being slightly distorted at room temperature (with bonds  $2 \times 1.982$  and  $4 \times 1.945$  Å) and AlO<sub>6</sub> octahedra being markedly distorted ( $3 \times 1.971$  and  $3 \times 1.852$  Å). In the case of TiO<sub>2</sub> the bond lengths at elevated temperatures will be calculated from lattice constants ( $a$  and  $c$ ) on the simplifying assumption that the crystallographic parameter  $u$  indicating the positions of oxygen atoms is temperature independent. As for Al<sub>2</sub>O<sub>3</sub> the Al–O distances will be used, determined by Aldebert and Traverse (8) with high-temperature neutron diffraction.

As results from the above discussion the coulombic-type  $s-R$  function is preferred to both power-type and exponential-type functions because it has a rationalized shape. This function will be therefore used in searching  $E-s-R$  relation. But for comparison  $E-s$  dependence will be examined also by using  $s$  calculated from Eq. (5).

TABLE I  
LATTICE PARAMETERS<sup>a</sup> OF THE STUDIED OXIDES AS  
FUNCTION OF TEMPERATURE

T (°C)	MgO a (Å)	CdO a (Å)	NiO a (Å)	TiO <sub>2</sub>	
				a (Å)	c (Å)
25	4.2128	4.6929	4.1770	4.5906	2.9568
50	4.2134	4.6934	—	—	—
100	4.2153	4.6962	4.1800	4.5916	2.9577
150	4.2174	4.6988	—	—	—
200	4.2200	4.7025	4.1863	4.5956	2.9606
250	4.2228	4.7056	—	—	—
300	4.2257	4.7092	4.1931	4.5997	2.9636
350	4.2280	4.7118	—	—	—
400	4.2311	4.7146	4.1989	4.6045	2.9680
450	4.2341	4.7188	—	—	—
500	4.2364	4.7221	4.2047	4.6072	2.9710
550	4.2396	—	—	—	—
600	4.2424	4.7298	4.2108	4.6102	2.9740
700	4.2489	4.7374	4.2167	4.6150	2.9781
800	—	—	4.2226	4.6187	2.9791
900	—	—	4.2283	4.6224	2.9840

<sup>a</sup> Accuracy of determination varied between 0.0003 and 0.0015.

These two procedures will be briefly designated as coulombic-version and power-version, respectively.

### Experimental

MgO, CdO, and TiO<sub>2</sub>-rutile used in this work were p.a. grade commercial oxides. NiO was obtained by pyrolysis of p.a. grade carbonate. Before further studies all oxides were preheated at 900–1000°C for several scores of hours. X-Ray diffraction patterns were obtained at 25–900°C with a DRON-2 diffractometer with CuK<sub>α</sub> (MgO, CdO, TiO<sub>2</sub>) or CrK<sub>α</sub> (NiO) radiation. At room temperature an internal standard of Al ( $a = 4.0494$  Å at 25°C) was used. Lattice parameters were calculated from the positions of 4–9 intense reflections from the range  $50^\circ < 2\theta < 140^\circ$ . Depending on resolution either  $\alpha$  or  $\alpha_1$  and  $\alpha_2$  lines were taken into account. The unit cell dimensions were refined with

a computer program involving the least-square method. The results obtained are gathered in Table I. Bond lengths were calculated in a way indicated in the previous paragraph. Bond strengths were calculated with Eqs. (5) and (7). Thermochemical data were taken from (9). All linear dependences discussed in this paper were determined with the least-squares method.

### Results and Conclusions

The determined  $E$ - $s$  dependences for all five studied oxides are shown in Figs. 1 and 2. They are linear in both coulombic- and power-versions in agreement with the hypothesis set up above. However, we also

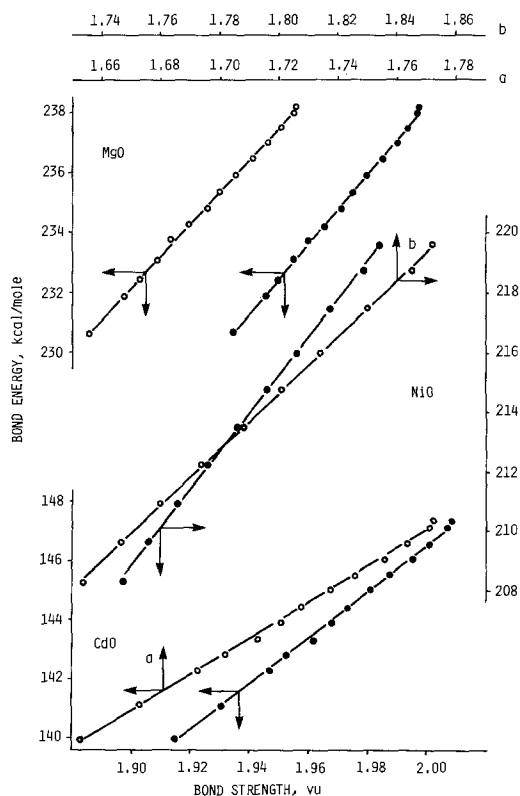


FIG. 1. Experimental bond-energy-bond-strength dependences for MgO, NiO, and CdO. Black points—coulombic-version ( $s$  from Eq. (7)), open points—power-version ( $s$  from Eq. (5)).

TABLE II  
 PARAMETERS CHARACTERIZING THE  $E$ - $R$  RELATIONSHIP<sup>a</sup>

Compound	$E_a^0$	"Theoretical" from Eq. (13)		Experimental from Eq. (18)					
		$J$	$E_0$	Coulombic-version			Power-version		
		$J$	$E_0$	$J$	$\delta$	$E_0$	$J$	$\delta$	$E_0$
MgO	238.2	119.1	0	117.0	1.8	4.4	106.4	10.6	30.1
CdO	147.4	73.7	0	78.4	6.4	-10.1	61.3	16.8	38.7
NiO	219.6	109.8	0	128.4	16.9	-35.1	94.5	13.9	44.6
TiO <sub>2</sub>	456.9	114.4	0	110.3	3.6	14.4	92.6	19.0	90.8
Al <sub>2</sub> O <sub>3</sub>	732.4	122.1	0	125.2	2.5	-35.0	100.1	18.0	121.8
C-O bonds	383.6	95.9	0	99.5	3.4	7.3	97.5	1.6	6.8

<sup>a</sup>  $E_a^0$  and  $E_a$  in kcal mole<sup>-1</sup>,  $J$  in kcal mole<sup>-1</sup> vu<sup>-1</sup>,  $\delta$  in %.

have to check if the  $E$ - $s$  lines pass through the origin.

As illustrated in Fig. 3 this requires a distant extrapolation which indicates that the experimental data fit rather the equation

$$E_a = J \sum_1^{mk} s_i + E_0 \quad (18)$$

with  $E_0 \neq 0$ . The determined, experimental parameters  $J$  and  $E_0$  are collected in Table II. The values of  $E_a^0$ , "theoretical"  $J$ 's resulting from Eq. (13) and deviations  $\delta = 100|J_{\text{theor}} - J_{\text{exp}}|/J_{\text{theor}}$  are also included. As seen from Table II experimental values of  $J$  for all five studied oxides in the coulombic-

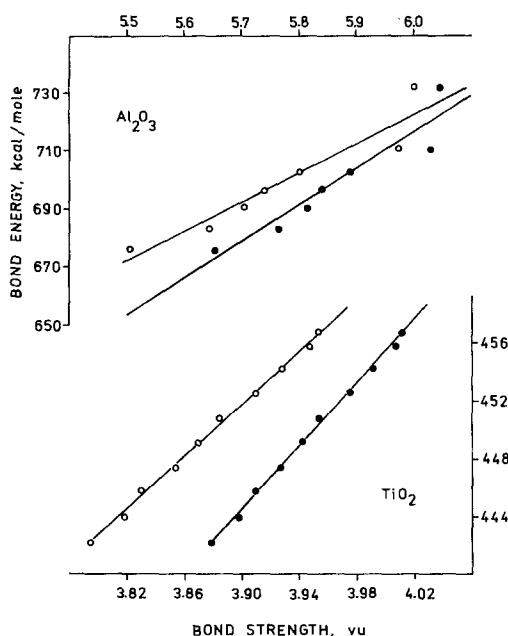


FIG. 2. Experimental bond-energy-bond-strength dependences for Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>. Black points—coulombic-version ( $s$  from Eq. (7)), open points—power-version ( $s$  from Eq. (5)).

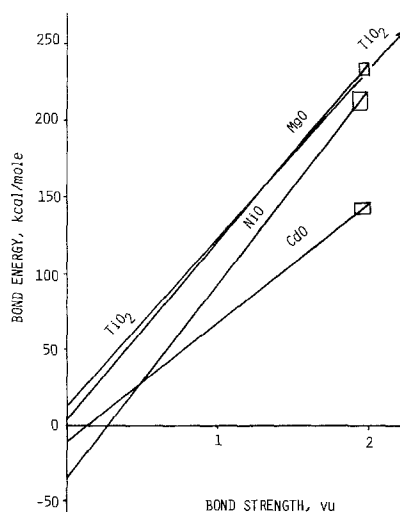


FIG. 3. Extrapolation of the  $E$ - $s$  lines in coulombic-version (cf. Figs. 1 and 2 and Table II) to the vicinity of the origin. Little rectangles recall the size of Fig. 1.

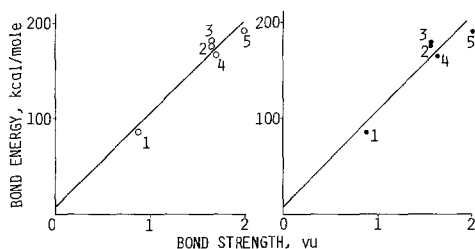


FIG. 4. Bond energy vs bond strength for C—O bonds. Black points—coulombic-version, open points—power-version. (1) Average C—O bond, (2) average C=O bond (aldehydes), (3) average C=O bond (ketones), (4) HCHO, (5) CO<sub>2</sub>. Bond lengths and energies from (10).

version are very close<sup>3</sup> to the “theoretical”  $J$ 's,  $|E_0|$  values are small,  $E_0$  being once positive, once negative. Taking into account the necessity of so distant an extrapolation these results may be considered as sufficient proof of the validity of Eq. (13) and the deviations of the  $E$ - $s$  lines from the origin may be ascribed to minor experimental errors in determining  $r_0$ , thermal expansion or thermochemical data.<sup>4</sup> This is not so in power-version where  $|E_0|$  values are always larger than those obtained in the coulombic-version, all  $E_0$  are positive, and  $\delta$ 's are either comparable with those from coulombic-version or, more frequently, significantly higher.

It may be useful to recall that the validity of Eq. (12) has been suggested for the first time in (7) on the basis of the bond-energy—bond-strength curve for C—O bonds in several types of organic molecules and in CO<sub>2</sub>. These data, recalculated in the analogous way as done for oxides are presented in

<sup>3</sup> The higher value of  $\delta$  observed for NiO may be due to the fact that the nature of its magnetic transformation at about 250°C (influencing  $C_p$ ) depends to some extent on the biography of a sample.

<sup>4</sup> Alternatively one may consider Eqs. (13) and (7) as a very good approximation of the real  $E$ - $s$ - $R$  dependence. Actually, the indicated equations are rationalized as a whole, but at present no explication of their numerator (Eq. (8)) can be offered.

Fig. 4 and included in Table II. As can be seen, the results obtained again confirm Eq. (12). For C—O bonds there is no essential difference between the coulombic- and power-versions.

The results obtained in this paper allow us to postulate that Eqs. (12)–(16) have general significance and reflect the bond-length—bond-energy dependence for all cations (atoms) forming bonds with oxygen in crystals as well as in molecules. The above considerations show also that  $C_p$  and the coefficient  $\alpha$  of thermal expansion are mutually related, but the shape of this relation is more difficult to be expressed in a general form<sup>5</sup> (among others due to the anisotropy). Although the validity of Eqs. (12)–(16) has been verified only for some simple oxides they should also be applicable for complex oxide crystals as they are based on Eq. (7) which has a general character (5). The application of the above-mentioned equations to a given cation—oxygen bond requires one to know  $r_0$  for the cation, which may be found in (5) and its  $J$  which may be calculated with Eq. (14) using accessible thermochemical data for the respective simple oxide containing the cation considered.  $J$  values for some cation—oxygen bonds are gathered in Table III. The proposed equations should find application in approximate thermochemical calculations for systems hardly accessible experimentally, involving in particular various problems concerning the surface of solids.

Recently (7, 11–16) one of us has proposed a new model of the structure and performance of catalytically active sites on surfaces of oxides (BSMAS = bond strength model of active sites). It is based on the conviction that the path of a catalytic reaction should be dependent on the geometric and energetic fit between the ad-

<sup>5</sup> The relation between  $C_p$  and  $\alpha$ , derived under some simplifying assumptions is known as Grüneisen's law.

TABLE III  
 $J$  [kcal mole<sup>-1</sup> vu<sup>-1</sup>] FACTORS FOR VARIOUS  
 CATION-OXYGEN BONDS

Ion	$J$	Ion	$J$	Ion	$J$
Ag <sup>1+</sup>	101.3	Ir <sup>4+</sup>	83.0	Rh <sup>3+</sup>	85.4
Al <sup>3+</sup>	122.1	K <sup>1+</sup>	83.7	S <sup>4+</sup>	61.7
Au <sup>3+</sup>	54.1	La <sup>3+</sup>	135.2	S <sup>6+</sup>	55.0
B <sup>3+</sup>	126.3	Li <sup>1+</sup>	139.7	Sc <sup>3+</sup>	135.7
Ba <sup>2+</sup>	122.3	Mg <sup>2+</sup>	119.1	Si <sup>4+</sup>	111.0
Be <sup>2+</sup>	141.1	Mn <sup>2+</sup>	109.3	Sm <sup>3+</sup>	116.9
Bi <sup>3+</sup>	69.1	Mn <sup>3+</sup>	90.3	Sn <sup>2+</sup>	100.1
C <sup>4+</sup>	95.6	Mn <sup>4+</sup>	77.6	Sn <sup>4+</sup>	82.5
Ca <sup>2+</sup>	126.6	Mn <sup>7+</sup>	51.8	Ta <sup>5+</sup>	116.0
Cd <sup>2+</sup>	73.7	Mo <sup>4+</sup>	104.4	Th <sup>4+</sup>	137.5
Co <sup>2+</sup>	109.1	Mo <sup>6+</sup>	85.9	Ti <sup>2+</sup>	147.8
Cr <sup>3+</sup>	106.4	N <sup>2+</sup>	61.8	Ti <sup>3+</sup>	127.6
Cr <sup>4+</sup>	88.3	N <sup>4+</sup>	49.2	Ti <sup>4+</sup>	114.2
Cr <sup>6+</sup>	68.7	N <sup>5+</sup>	46.3	Tl <sup>1+</sup>	94.2
Cs <sup>1+</sup>	86.5	Na <sup>1+</sup>	106.5	U <sup>4+</sup>	123.3
Cu <sup>1+</sup>	130.5	Ni <sup>2+</sup>	109.8	U <sup>6+</sup>	98.0
Cu <sup>2+</sup>	88.7	Pb <sup>2+</sup>	79.4	V <sup>2+</sup>	142.2
Fe <sup>2+</sup>	109.0	Pb <sup>4+</sup>	58.0	V <sup>3+</sup>	119.2
Fe <sup>3+</sup>	94.2	Pd <sup>2+</sup>	85.7	V <sup>4+</sup>	103.1
Ga <sup>3+</sup>	95.7	Pu <sup>4+</sup>	114.0	V <sup>5+</sup>	91.4
Ge <sup>4+</sup>	83.2	Rb <sup>1+</sup>	90.1	W <sup>4+</sup>	115.7
H <sup>1+</sup>	116.0	Re <sup>4+</sup>	101.7	W <sup>6+</sup>	97.2
Hf <sup>4+</sup>	132.8	Re <sup>6+</sup>	85.1	Y <sup>3+</sup>	139.5
Hg <sup>2+</sup>	37.8	Re <sup>7+</sup>	77.6	Zn <sup>2+</sup>	86.9
In <sup>3+</sup>	86.1	Rh <sup>2+</sup>	136.8	Zr <sup>4+</sup>	131.2

sorbed molecule and the neighborhood of the adsorption site. In this model structural considerations are based on crystallographic data<sup>6</sup> and bond strength has been arbitrarily assumed to be a measure of binding energy. BSMAS has already been applied to explain (7, 11-14) and to predict (15, 16) a number of catalytic reactions. Now, all conclusions based on BSMAS can be translated into actual energy units. This was in fact the original inspiration and aim of the present work, though the proposed

<sup>6</sup> This was done so because the considered catalytic reactions were carried out on the well-defined morphological planes of monocrystalline catalyst grains. Generally structural considerations may be also based on adequate experimental data obtained, e.g., with EXAFS (17, 18).

$E$ - $R$  relationship may be useful in many other fields.

It should not be forgotten, however, that Eqs. (12)-(16) still have an empirical character and therefore their precision is limited. An example of such limitation is given in Table IV where  $E_{a,comp}^0$  calculated for a number of oxide compounds are compared with  $E_{a,ox}^0$  expressing the atomization energies of the constituent oxides taken in the quantities equivalent to the compounds considered. Both  $E_{a,comp}^0$  and  $E_{a,ox}^0$  were calculated with Eqs. (13) and (7) by extending the sums over all chemically and structurally nonequivalent cations and using the respective  $J$ 's. As the thermodynamically stable compounds are considered  $\Delta = (E_{a,comp}^0 - E_{a,ox}^0)$ , reflecting the standard heat of formation from oxides should be positive. A perplexing finding is that  $\Delta$ 's are systematically negative (with one exception only). This means that the numerical coefficients in Eq. (7) are inaccurate. Let us note, however, that the heats of formation from

TABLE IV  
 CALCULATED STANDARD ATOMIZATION ENERGIES  
 $E_{a,comp}^0$  OF SOME CRYSTALS COMPARED WITH  
 STANDARD ATOMIZATION ENERGIES  $E_{a,ox}^0$  OF THEIR  
 CONSTITUENT OXIDES ( $\Delta = E_{a,comp}^0 - E_{a,ox}^0$ )<sup>a</sup>

Compound	$E_{a,comp}^0$	$E_{a,ox}^0$	$\Delta$	Source of structural data
MgAl <sub>2</sub> O <sub>4</sub>	950.7	970.2	-19.5	(19)
ZnAl <sub>2</sub> O <sub>4</sub>	908.4	905.8	+2.6	(19)
CoAl <sub>2</sub> O <sub>4</sub>	949.5	950.2	-0.7	(19)
FeAl <sub>2</sub> O <sub>4</sub>	941.2	950.0	-8.8	(19)
MgCr <sub>2</sub> O <sub>4</sub>	850.1	876.6	-25.5	(19)
MgV <sub>2</sub> O <sub>6</sub>	1119.3	1152.2	-32.9	(20)
CdV <sub>2</sub> O <sub>6</sub>	1044.0	1161.4	-17.0	(21)
CuV <sub>2</sub> O <sub>6</sub>	1084.8	1091.6	-6.8	(22)
Zn <sub>2</sub> V <sub>2</sub> O <sub>7</sub>	1191.1	1261.6	-70.5	(23)
CdV <sub>2</sub> O <sub>7</sub>	1159.9	1208.8	-48.9	(24)
CuWO <sub>4</sub>	749.6	760.6	-11.0	(25)
CoMoO <sub>4</sub>	729.6	733.6	-4.0	(26)
CuMoO <sub>4</sub>	651.5	692.8	-41.3	(27)

<sup>a</sup> All energies in kcal mole<sup>-1</sup>.

oxides of  $\text{MgAl}_2\text{O}_4$ ,  $\text{MgCr}_2\text{O}_4$ , and  $\text{FeAl}_2\text{O}_4$  are  $6 \pm 3$ ,  $5 \pm 3$ , and  $10 \pm 1$  kcal mole<sup>-1</sup>, respectively. This means that the error in determining the atomization energies of the above-quoted spinels amounts only to 2–3.5%.<sup>7</sup> In the worst case of  $\text{Zn}_2\text{V}_2\text{O}_7$  the estimated error is less than 10%.

The examples considered in this paper allow us to conclude that the proposed  $E$ – $R$  relationship is sufficiently accurate to compare the relative differences between various bonds in a given crystal and their changes with temperature. On the other hand, it is yet not accurate enough to determine the heats of formation.

The examples considered above, together with the results of paper (5), allow us to conclude also that applications of the bond strength in the analysis of crystal structures in the way used so far have a questionable ground. As frequently pointed out, e.g., in (3), the bond strengths so far reported have the property that their sum around each atom is within about 5% of its valence. Such accuracy is insufficient in some cases. An error of 5% corresponds in the energetic scale to about 5 kcal mole<sup>-1</sup> vu<sup>-1</sup> (cf. Table III). This is comparable with heats of formation of complex oxide compounds from simple oxides as well as with changes in  $E_a$  corresponding to heating a crystal by several hundred degrees. Simultaneously the high percentage of  $s$  (or  $E_a$ ), comprising the heat of formation of simple oxide and heats of atomization of the constituent elements, is structure insensitive from the viewpoint of the complex oxide compound. Due to this fact bond strength sums determined with an accuracy of about 5% are useful only to detect either relative or absolute, but rough enough effects. The tolerance of 5% has also disguised so far the necessity to choose a standard state for the

bond strength without which all fine effects are the more so difficult to be distinguished.

The results shown in Table IV suggest that the expected accuracy of the presently proposed Eqs. (7) and (12)–(16) is also within about 5%. This limits their applications to the cases indicated above (relative differences of various bonds in the same structure). Simultaneously, however, the present and the former (5) papers indicate the reasons for the above-mentioned inaccuracies and therefore they may serve as an inspiration to seek a more exact  $E$ – $R$  relationship, which would be highly desirable.

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*Note added in proof.* In the preceding paper (5) the new scale of the absolute ionic radii  $\rho_0$  has been proposed;  $\rho_0 = r_0 + h$  for the cations and  $\rho'_0 = r'_0 - h$  for the anions ( $h = 0.499$ ). If this new scale is used Eqs. (15) and (16) remain valid,  $R_0$  and  $d$  are numerically the same but consequently they should be expressed as:  $R_0 = \rho_0 + \rho'_0$  and  $d = 0.1350 - 0.0056z - 0.0347\rho_0 - 0.0050z\rho_0$ .

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<sup>7</sup> Example:  $E_{a,ox}^0$  for  $\text{MgAl}_2\text{O}_4$  is 970.2;  $E_{a,comp}^0$  should be  $970.2 + 6 = 976.2$  instead of 950.7;  $976.2 - 950.7 = 25.5$  which makes 2.6%.



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