

Brief Report

The Bulk Modulus-Volume Relationship for Oxides ^{1, 2}

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The relationship $KV_0 = \text{constant}$ is shown to hold for oxides as well as for alkali halides. The product of bulk modulus and volume depends on the crystal structure, valance product, and a repulsive parameter. The exponential repulsive parameter ρ is calculated for oxides in the halite, wurtzite, corundum, spinel, perovskite, and rutile structures for which elastic constant data are available. This parameter satisfies the relationship $\rho = 0.05 (1 + R + 3\Delta R)$ where R is the cube root of the molecular volume and ΔR is the difference between R and the radius of the small cation. The reduced Madelung constant $\alpha = A/mz_1z_2$ (where A is the conventional Madelung constant, z_1z_2 is the valance product, and m is the number of ions in the chemical formula) satisfies the relation $\alpha = 0.20 + 0.45\Delta R$. The calculated values for the bulk modulus and the repulsive parameter can be used to estimate densities at pressures of a megabar with an accuracy of about 1%.

The fact that the value of the ambient bulk modulus of solids K is controlled primarily by the specific volume at ambient conditions has been noted by many. *O. L. Anderson and Nafe [1965]* showed that the bulk modulus K was very nearly inversely proportional to the specific volume V_0 for alkali halides, fluorides, selenides, sulfides, and covalent compounds. *Don L. Anderson [1967]* reached a similar conclusion for oxides and silicates, as did *O. L. Anderson and Soga [1967]* for a sequence of four diatomic oxides.

For any solid where the potential U can be separated into an attractive term and a repulsive term, which are functions of the interatomic separation r , we can write

$$U = U_a(r) + f(r) \quad (1)$$

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² Lamont-Doherty Geological Observatory Contribution No. 1512.

For an ionic crystal with a Born power law repulsive potential, it can be shown that

$$KV_0 = Az_1z_2e^2(n - 1)/9r_0 \quad (2)$$

where n is the exponent in the power law repulsive potential. If the exponential form of the repulsive potential is used, the energy per cell can be written

$$U(r) = -A/4 + Be^{-r/\rho} \quad (3)$$

At equilibrium the bulk modulus-volume product can be written

$$KV_0 = Az_1z_2e^2(r_0/\rho - 2)/9r_0 \quad (4)$$

In most of the subsequent discussion we will restrict our attention to the exponential form. The parameter n in the power law potential is simply related to ρ ;

$$n = (r_0/\rho) - 1 \quad (5)$$

Data for a number of oxides are presented in Table 1 and Figure 1, which demonstrates that KV_0 is a constant for a large variety of oxide compounds. Here V_0 is the specific molar volume

TABLE 1. Data for Calculation of Repulsive Range Parameter

Substance	Structure	$\langle z_c z_a \rangle$	$V, \text{\AA}^3$	$R, \text{\AA}$	A_R	α	K, Mb	$\rho, \text{\AA}$	ψ
MgO	halite	4	18.67	2.653	8.808	1.10	1.622	0.477	0.164
CaO	halite	4	27.83	3.030	8.808	1.10	1.059	0.509	0.160
*BaO	halite	4	42.118	3.479	(8.808)	(1.10)	(0.666)	(0.55)	...
SrO	halite	4	34.351	3.251	8.808	1.10	0.840	0.54	...
BeO	wurtzite	4	13.77	2.397	9.504	1.19	2.196	0.482	0.164
ZnO	wurtzite	4	23.74	2.874	9.604	1.20	1.394	0.490	0.179
MgAl ₂ O ₄	spinel	5.33	65.94	4.040	67.54	1.81	2.020	0.790	0.155
FeFe ₂ O ₄	spinel	5.33	73.85	4.195	65.48	1.75	1.872	0.769	0.161
NiFe ₂ O ₄	spinel	5.33	72.48	4.169	65.53	1.76	1.823	0.790	0.153
MnFe ₂ O ₄	spinel	5.33	76.72	4.249	(66.7)	(1.79)	1.851	0.768	0.165
*Ni ₂ SiO ₄	spinel	5.33	65.04	4.022	(72.1)	(1.93)	(2.13)	(0.803)	...
*Fe ₂ SiO ₄	spinel	5.33	69.78	4.117	(72.2)	(1.94)	(1.94)	(0.822)	...
*Mg ₂ SiO ₄	spinel	5.33	65.817	4.038	(65.5)	(1.76)	(1.901)	(0.81)	...
SrTiO ₃	perovskite	6	59.558	3.905	49.51	1.65	1.787	(0.74)	0.154
Al ₂ O ₃	corundum	6	42.47	3.489	45.77	1.53	2.515	0.674	0.154
Fe ₂ O ₃	corundum	6	50.27	3.691	45.68	1.52	2.066	0.700	0.150
Cr ₂ O ₃	corundum	6	48.12	3.637	(45.7)	(1.52)	2.237	0.681	0.155
SiO ₂	rutile	8	23.27	2.855	(30.9)	(1.29)	3.6	0.569	0.151
TiO ₂	rutile	8	31.23	3.149	30.89	1.29	2.24	0.658	0.126

* predicted

of the formula, and K is the bulk modulus at zero pressure.

MgO, CaO, and NiO have the rocksalt structure with 6-6 coordination; ZnO and BeO have the wurtzite structure with 4-4 coordination. BeO, ZnO, and NiO all have lower ionicities than the other compounds. Nickel oxide has an anomalously high Poisson's ratio (0.416), which is probably related to the fact that it is in the anti-ferromagnetic state at room temperature [Liebermann, 1969]. The data on SrO is from Johnson *et al.* [1970].

The corundum, or M_2O_3 line, is well determined by Al_2O_3 , Fe_2O_3 , and Cr_2O_3 . There is also fair consistency among the spinels M_3O_4 . Zircon, $ZrSiO_4$, although of quite different structure, ionicity, and valency than the spinels, also falls close to the M_3O_4 line. The MO_2 line is poorly determined and is shown dashed. The MO_2 compounds, SiO_2 (stishovite), and TiO_2 are both in the rutile structure, and both are only about 50% ionic. A recent redetermination of the bulk modulus of stishovite from X-ray compression and shock wave studies gives 3.0 Mb (Ahrens and Takahashi, personal communication), a value that falls on the dashed line. No line is drawn for the wurtzite structures (BeO, ZnO); they accidentally fall on the lines for unrelated structures.

The data plotted on the nickel ferrite and hematite lines support the conclusion given by *O. L. Anderson and Soga* [1967] that classes of oxides with isomorphic electronic structures would follow the $KV_0 = \text{constant}$ law. The uncertainty raised by Anderson and Soga on iron-rich compounds now appears solved.

The -1 slope of the lines is at this point entirely empirical, and it is amazing that it satisfies so many groups of data. The small deviations of the measured values of K from the relation $KV_0 = \text{constant}$ are systematic, and this will be discussed below.

The parameter $\psi = KV_0/(z_c z_a e^2)$ is tabulated in the last column of Table 1. Except for ZnO and TiO_2 all of the values fall in the range 0.150-0.165 and the values show no systematic behavior. ZnO and TiO_2 are anomalous in several other respects. The values of Poisson's ratio are high, the shear velocity decreases with pressure, and the oxygen coordination is anomalous for the size of the cation. We are, therefore, not too concerned that they do not fit the pattern well. If these compounds are excluded, the remaining substances for which bulk modulus data are available satisfy

$$\psi = 0.157 \pm 0.005 \quad (6)$$

The standard deviation corresponds to an error

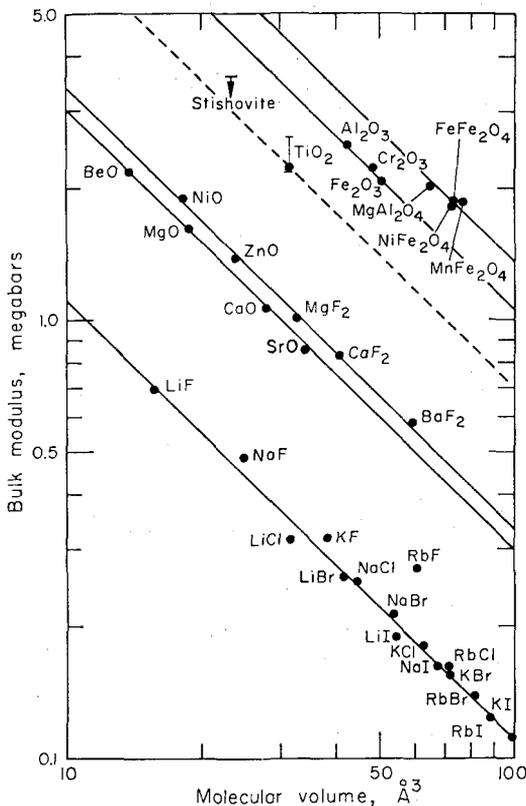


Fig. 1. Bulk modulus versus molecular volume for halides and oxides in the rocksalt (alkali-halides, MgO, CaO, NiO), calcium difluoride (MgF_2 , CaF_2 , BaF_2), rutile (TiO_2 , SiO_2), corundum (Al_2O_3 , Cr_2O_3 , Fe_2O_3) and spinel (MgAl_2O_4 , Fe_3O_4 , NiFe_2O_4 , MnFe_2O_4) structures. No line is drawn for the wurtzite structure compounds (BeO , ZnO). The proximity of NiO and ZnO to the MF_2 line is accidental.

of 3.3%. This is remarkable consistency when one considers that so many structures (halite, wurtzite, spinel, corundum, perovskite, and rutile) and so many cations (Mg, Be, Al, Fe^{+2} , Fe^{+3} , Mn, Ni, Cr, Sr, and Si) are involved, and that no account has been taken of structural factors (the Madelung constant) or range or repulsion parameters. These factors apparently tend to compensate for each other.

Uncertainties in the bulk modulus should be mentioned here. Although we have tried to select the most accurate ultrasonic data in constructing Table 1, there is still the possibility of error in the bulk modulus. For example, using the compilation of *O. L. Anderson et al.* [1968] and Schreiber (personal communication regard-

ing new measurements on stoichiometric spinel), we find the following range in values for the bulk modulus in kilobars: MgO $1619 \pm 3.2\%$ (16 measurements); ZnO , $1414 \pm 1.2\%$ (3 measurements); Al_2O_3 , $2518 \pm 1\%$ (8 measurements); MgAl_2O_4 , $1941 \pm 1.6\%$ (3 measurements); BeO , $2,620 \pm 24\%$ (3 measurements); and TiO_2 , $2,098 \pm 2.3\%$ (4 measurements). Specimen quality, bond and transducer corrections, errors in the VRH averaging scheme for obtaining the bulk modulus from single crystal data for non-cubic crystals, and the effect of porosity and anisotropy on sintered aggregates are probably all involved in the discrepancies. Ultrasonic data are not available for stishovite and the tabulated value can be in error by more than 10%. Equation 6 can, therefore, be used to estimate the bulk modulus of close-packed oxides with an uncertainty not much greater than the range of experimental determinations.

The empirical repulsive range parameter ρ calculated from the data in Table 1 and equation 4 is tabulated in the next to last column in Table 1. It is relatively constant for each group of compounds and shows a tendency to increase with molecular volume. It can be well approximated, as shown in Table 2, by the simple equation

$$\rho_c = 0.05(1 + R + 3\Delta R) \quad (7)$$

where R is the cube root of the molecular volume and $\Delta R = R_c$, where R_c is the (Pauling) radius of the smallest cation. Equally satisfactory relations can be found between ρ and other measures of the crystal and ionic dimensions. Equation 5 can be used to estimate the power law repulsive parameter n .

The reduced Madelung constant α , also given in Table 1, is defined as

$$\alpha = A/m\langle z_c z_a \rangle \quad (8)$$

where m is the number of ions in the chemical formula. This is a useful parameter since it varies much less from structure to structure [Templeton, 1953] than the conventional Madelung constant, and it correlates well with coordination and interatomic distances. For example, it satisfies the relation

$$\alpha_c = 0.20 + 0.45 \Delta R \quad (9)$$

as shown in Table 2.

For crystals involving more than one cation

TABLE 2. Comparison of Repulsive Parameter

Calculated from $\rho_c = 0.05(1 + R + 3 \Delta R)$ where $\Delta R = R - R_c$ with that calculated from the bulk modulus. Also given are the reduced Madelung constants calculated from $\alpha_c = 0.20 + 0.45\Delta R$, the reduced Madelung constant calculated by conventional techniques, and the error.

	R_c	R	ρ_c	ρ	error	ΔR	α_c	α	error
MgO	0.65	2.65	0.48	0.48	0.00	2.00	1.10	1.10	0.00
CaO	0.99	3.03	0.51	0.51	0.00	2.04	1.12	1.10	0.02
BeO	0.31	2.40	0.48	0.48	0.00	2.09	1.14	1.19	-0.05
ZnO	0.74	2.82	0.50	0.49	0.01	2.08	1.14	1.20	-0.06
MgAl ₂ O ₄	0.50	4.04	0.78	0.79	-0.01	3.54	1.79	1.81	-0.02
FeFe ₂ O ₄	0.64	4.20	0.79	0.77	0.02	3.56	1.80	1.75	0.05
NiFe ₂ O ₄	0.64	4.17	0.79	0.79	0.00	3.53	1.79	1.76	0.03
MnFe ₂ O ₄	0.64	4.25	0.80	0.77	0.03	3.61	1.82	1.79	0.03
Ni ₂ SiO ₄	0.41	4.022	(0.80)*						
Fe ₂ SiO ₄	0.41	4.117	(0.82)*						
Mg ₂ SiO ₄ (sp)	0.41	4.038	(0.81)*						
Al ₂ O ₃	0.50	3.49	0.67	0.67	0.00	2.99	1.55	1.53	0.02
Fe ₂ O ₃	0.64	3.69	0.69	0.70	-0.01	3.05	1.57	1.52	0.05
Cr ₂ O ₃	0.69	3.64	0.67	0.68	-0.01	2.95	1.53	(1.52)	-0.01
SiO ₂	0.41	2.86	0.56	0.57	-0.01	2.45	1.20	(1.29)	0.09
TiO ₂	0.68	3.15	0.58	0.66	-0.08	2.47	1.31	1.29	0.03
SrTiO ₃	0.68	3.91	0.73	0.74	-0.01	3.23	1.65	1.65	0.00

* Predictions.

the valence product is defined as

$$z_c z_a = \sum^p x_i z_i z_a / p$$

where x_i is the number of cations in the formula having valence z_i , z_a is the valence of the anion (oxygen), and p is the total number of cations in the formula.

The empirical relations found for ρ and α permit the bulk modulus to be estimated from equation 6 knowing only the valence product and the molecular volume of the crystal. The bulk modulus K_c calculated in this way is given in Table 3. Excluding ZnO and TiO₂, the per cent standard deviation between computed and measured bulk moduli is 3%. It appears, therefore, that the bulk modulus of simple close-packed oxides can be estimated to a useful degree of accuracy from the simple relationships in this paper.

In Table 1 predictions are made for the spinels Ni₂SiO₄, Fe₂SiO₄, and Mg₂SiO₄. For these compounds the Madelung constant can be calculated from the crystal structure, and only the range parameter need be calculated from an

empirical relationship. The values of 2.13 Mb and 1.94 Mb calculated for the adiabatic bulk moduli of Ni₂SiO₄ and Fe₂SiO₄ spinels can be compared with the (isothermal) values of 2.11 ± 0.3 Mb and 2.12 ± 0.1 Mb, respectively, determined by Mao [1967]. Values for BaO and SrO are also predicted.

Open-packed silicates are another matter. The strength of the Si-O bond, its relative constant length in the low-pressure phases of silicates, and its covalency suggest that the simple ideas expressed in this paper will not be adequate to treat these open-packed structures. Madelung constants also are not available for such important silicates as olivines, pyroxenes, garnets, etc. A few preliminary calculations using the empirical Madelung constant suggest that the range parameter is very large (>1 Å) for these silicates. For α -quartz, ρ is 1.34 Å. There is also reason to believe that these structures do not deform isostructurally and, therefore, bond-bending and non-centrosymmetric forces may be important. To some extent this is also true of some of the structures discussed in this paper, particularly stishovite and rutile.

TABLE 3. Comparison of Computed K_c and Measured K Bulk Modulus

	$\langle z_c z_o \rangle$	V	R	ρ_c	α_c	K_c	K	Error, %	
MgO	4	18.67	2.653	0.48	1.10	1.61	1.62	-0.01	-0.6
CaO	4	27.83	3.030	0.51	1.12	1.07	1.06	0.01	+0.9
BeO	4	13.77	2.397	0.48	1.14	2.12	2.20	-0.08	-3.6
ZnO	4	23.74	2.874	0.50	1.14	1.28	1.39	-0.11	-7.9
MgAl ₂ O ₄	5.33	65.94	4.040	0.78	1.79	2.04	2.02	0.02	+0.1
FeFe ₂ O ₄	5.33	73.85	4.195	0.79	1.80	1.84	1.87	-0.03	-1.6
NiFe ₂ O ₄	5.33	72.48	4.169	0.79	1.79	1.86	1.82	+0.04	+2.2
MnFe ₂ O ₄	5.33	76.72	4.249	0.80	1.82	1.77	1.85	-0.08	-4.3
SrTiO ₃	6	59.56	3.905	0.73	1.65	1.83	1.79	+0.04	+2.2
Al ₂ O ₃	6	42.47	3.489	0.67	1.55	2.58	2.52	+0.06	+2.4
Fe ₂ O ₃	6	50.27	3.691	0.69	1.57	2.18	2.07	+0.11	+5.3
Cr ₂ O ₃	6	48.12	3.637	0.67	1.53	2.30	2.24	+0.06	+2.7
SiO ₂	8	23.27	2.855	0.56	1.20	3.44	3.6	-0.16	-4.4
TiO ₂	8	31.23	3.149	0.58	1.31	2.81	2.24	+0.57	+25.4

As shown above, the repulsive parameter n or ρ can be calculated from the zero-pressure parameters V_0 and K_0 . A critical test of the form of the repulsive potential is available from compression and shock wave measurements. The equation of state for the power law and exponential forms of the repulsive potential are, respectively,

$$P = \frac{3K_0}{n-1} \left[\left(\frac{V_0}{V} \right)^{4/3} - \left(\frac{V_0}{V} \right)^{n+3/3} \right] \quad (10)$$

$$P = \frac{3K_0}{r_0/\rho - 2} \left[\left(\frac{V_0}{V} \right)^{4/3} - \left(\frac{V_0}{V} \right)^{2/3} e^{r_0/\rho} e^{-r/\rho} \right] \quad (11)$$

Equations 10 and 11 have been used to estimate the pressures at high compression on MgO and Al₂O₃ using the zero-pressure bulk modulus K_0 and repulsive parameters from Table 1. Ahrens *et al.* [1969] computed pressures on the room temperatures adiabats for these materials from shock wave data. For $V_0/V = 1.4$ the pressure is computed to be 1050 kb from equation 11 and 950 kb from equation 12. The 'measured' value is about 1050 kb. The estimated values for K_c , ρ_c , and n from Table 3 and equation 7 give corresponding values for the pressure of 1010 and 960 kb, respectively. For Al₂O₃ at a compression of $V_0/V = 1.20$, the estimated pressure on the adiabat is about 900 kb. The power law poten-

tial gives 850 kb, and the exponential gives 790 kb. The corresponding values of pressure calculated from K_c and ρ_c are 870 and 840 kb. At these pressures an error of 50 kb in pressure corresponds to an error of about 0.04 g/cm³ in density, less than 1%. Considering that the effects of thermal pressure have been ignored in the calculations and only allowed for approximately in the 'measurements,' the agreement at such large compressions is satisfactory. The power law form of the repulsive potential seems to be slightly preferred over the exponential form.

Another check on the form of the repulsive potential is available from ultrasonic measurements of dK/dP . This quantity depends only on the parameters in the repulsive potential; that is,

$$(dK/dP)_0 = (n+7)/3 \quad (12)$$

$$(dK/dP)_0 = [3(2 - r_0/\rho)]^{-1}$$

$$\cdot [14 - (1 + r_0/\rho)(2 + r_0/\rho)] \quad (13)$$

for the power law and exponential forms respectively. Table 3 gives $(dK/dP)_0$ evaluated from equations 12 and 13 and, for comparison, the ultrasonic results. Again the power law repulsive potential gives better agreement although the measured values of $(dK/dP)_0$ are higher than computed for either potential. The

TABLE 4. Repulsive Parameters and Corresponding Values of dK/dP for Power Law and Exponential Repulsive Potentials

Substance	r_0/ρ	dK/dP	n	dK/dP	$(dK/dP)_{exp}^*$
MgO	5.56	3.33	4.56	3.85	4.50
CaO	5.95	3.48	4.95	3.98	5.23
BeO	4.97	3.10	3.97	3.66	5.52
ZnO	5.87	3.45	4.87	3.96	4.78
MgAl ₂ O ₄	5.11	3.16	4.11	3.70	4.18
NiFe ₂ O ₄	5.28	3.22	4.28	3.76	4.41
Al ₂ O ₃	5.18	3.18	4.18	3.73	3.98
Fe ₂ O ₃	5.27	3.22	4.27	3.76	4.53
SiO ₂ (st.)	5.02	3.12	4.02	3.67	7
TiO ₂	4.79	3.02	3.79	3.60	6.76

* Experimental results from Anderson et al. [1968], Liebermann [1969], Manghani [1969], and Ahrens et al. [1969].

exponential form gives $(dK/dP)_0$ from 0.50 to 0.58 units lower than the power law form.

Spetzler [1970] measured the elastic properties of single and polycrystal MgO and the temperature and pressure derivatives of the elastic properties. He used a pseudoresonance ultrasonic technique with a buffer rod in order to avoid the necessity for a bond or transducer correction. At room temperature he found $(dK/dP)_0$ of 3.85 for single crystal MgO, which is in excellent agreement with the value computed with the power law potential. The experimental values in Table 3 were all measured with the transducer bonded directly to the specimen. Spetzler and Don L. Anderson (in preparation) show that dK/dP measured by conventional techniques will be an upper bound to the actual dK/dP . In addition to these experimental uncertainties, we should stress that the comparisons we have been making should actually be made at 0° since we are making no explicit allowance for temperature.

In light of the above comment, and considering the extremely simplified nature of the perfectly ionic centrosymmetric force model, and considering the assumption of isostructural deformation, we consider the above tests to be encouraging, particularly when it is remembered that we have used only one disposable parameter. The most serious discrepancies occur for rutile and stishovite where directional forces and bond-bending phenomena are most likely.

Don L. Anderson [1969] noted that the ratio of the bulk modulus and the density for com-

plex oxides could be well approximated by a molecular average of the corresponding ratio of the component oxides. This ratio, the seismic parameter Φ , was computed for 13 oxides for which data on the compound and the component oxides were available; the average error was 4%. An additional test is now possible using the data for $\alpha\text{Fe}_2\text{O}_3$, NiFe₂O₄ [Liebermann, 1970] and NiO [Notis, 1969]. Taking $\Phi(\text{NiO}) = 27.9$ (km/sec)² and $\Phi(\alpha\text{Fe}_2\text{O}_3) = 39.3$ (km/sec)², we obtain

$$\begin{aligned}\Phi(\text{NiFe}_2\text{O}_4) &= [\Phi(\text{NiO}) + \Phi(\text{Fe}_2\text{O}_3)]/2 \\ &= 33.6 \text{ (km/sec)}^2\end{aligned}$$

The measured value [Liebermann, 1970] is $\Phi(\text{NiFe}_2\text{O}_4) = 34.3$ (km/sec)², which is within 2% of that predicted. This is further confirmation of the Φ averaging scheme.

In summary, we find that the $KV_0 = \text{constant}$ law holds well for all classes of oxides where there is a sequence of compounds in an isomorphic electronic structure. The value of the constant depends upon the valence product and ionicity; the latter parameter in the present paper is absorbed in the repulsive parameter.

We also find additional confirmation of additivity in the seismic Φ law.

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