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ABSTRACT

Madelung constants are given for 38 structures, some of which are relatively complex. Those of binary compounds are compared with a previous empirical correlation.

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During a series of calculations of the variation of lattice energy with respect to atomic parameters,[1] we have incidentally calculated many Madelung constants of known structures. These constants are reported here in the hope that other workers will find them useful.

The calculations were made with the IBM-704 computer according to Bertaut's method[2] with correction for series termination.[3] Some details of the computer program are described elsewhere.[4]

The structures, together with the values of the parameters that were used, are given in Table I. (The obvious cubic structures without parameters are not listed.) This table gives the chemical formula of the compound, the space group, the cell constants (a, b, c, β), the symbol for the first element followed by its Wycoff symmetry as described in the International Tables,[5] the x, y, and z parameters, the symbol of the second element, etc. If the cell constants b, c, β and the x, y, z parameters are not necessary, no entry is made, and the next piece of information is listed.

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For example, consider β LaOF. The space group is $R\bar{3}m$, a = 4.0507 A, c = 20.213 A; lanthanum is in Wycoff symmetry c, with x = 0.242; oxygen is in Wycoff symmetry c with x = 0.122; and fluorine is also in Wycoff symmetry c with x = 0.370. No exhaustive survey of the literature was made in order to ascertain the latest values of the parameters.

The results of the calculations are given in Table II. The shortest interatomic distance is denoted by R_0. In many cases more digits are listed than have chemical significance in order to assure that (except in cubic cases) the mathematics is not the determining factor in the accuracy with which the Madelung constant is known. The second entry in Table II is the series termination correction for the Madelung constant. The Madelung constant based on R_0 as unit distance is denoted $A(R_0)$. Care should be exercised so that this is not mistaken for the Madelung constant based on the average shortest distance. For certain applications, this latter has more significance; it may readily be computed by multiplying the sixth entry in Table II, $\langle R \rangle$, by $A(R_0)$ and dividing by R_0. The sixth entry in this table, $\langle R \rangle$, was determined by taking the average distance of the p_c nearest neighbors of the cation.

The fourth entry, β/π, is a measure of where the series was terminated.[3] Because of the sensitivity of the Madelung constant to changes in the values of the structural parameters, no conscious effort was made to carry most of the calculations past a meaningful number of digits. Experience has shown that the last digit of $A(R_0)$ as listed here must be considered to be known with the accuracy of ± 1. This can be verified by comparison of the results for CaF_2, CsCl, Cu_2O, NaCl, and ZnS with more accurate values already published.[6] The values for the two CdI_2 structures confirm the results of Hartman[7] rather than the earlier values quoted by Sherman.[8]

Table I. Description of structures for which Madelung constants were calculated

Compound	Structure
$AlCl_3$	C2/m; 5.93, 10.24, 6.17, 108°; Al-g, 0.167; Cl-i, 0.226, 0.219; Cl-j, 0.250, 0.175, 0.781
αAl_2O_3	$R\bar{3}c$; 4.7628, 13.0082; Al-c, 0.355; O-e, 0.303
$BeCl_2$	Ibam; 9.86, 5.36, 5.26; Be-a; Cl-j, 0.109, 0.203
BeO	$P6_3mc$; 2.698, 4.380; Be-b, (0.0); O-b, 0.365
BiSCl	Pnma; 7.70, 4.00, 9.87; Bi-c, 0.140, 0.138; S-c, 0.77, 0.04; Cl-c, 0.50, 0.79
$CaCl_2$	Pnnm; 6.25, 6.44, 4.21; Ca-a; Cl-g, 0.275, 0.325
$CaTiO_3$ (a)	Pm3m; 3.84; Ca-a; Ti-b; O-c
$CdCl_2$	$R\bar{3}m$; 3.86, 17.50; Cd-a; Cl-c, 0.25
CdI_2(Bozorth)	$P\bar{3}m1$; 4.240, 6.855; Cd-a; I-d, 0.25
CdI_2(Hassel)	$P6_3mc$; 4.240, 13.710; Cd-b, 0.00; I-b, 0.625; I-a, 0.375
$LaCl_3$	$P6_3/m$; 7.483, 4.375; La-d; Cl-h, 0.287, 0.382
LaF_3	$P6_3/mmc$; 4.148, 7.354; La-c; F-b; F-f, 0.57
La_2O_3	$P\bar{3}m1$; 3.9373, 6.1299; La-d, 0.245; O-a; O-d, 0.645
LaOCl	P4/nmm; 4.119, 6.883; La-c, 0.178; O-a; Cl-c, 0.635
βLaOF	$R\bar{3}m$; 4.0507, 20.213; La-c, 242; O-c, 0.122; F-c, 0.370
γLaOF	P4/nmm; 4.091, 5.837; La-c, 0.778; O-a; F-b
$MgAl_2O_4$	Fd3m; 8.0800; Mg-a; Al-d; O-e, 0.387
MgF_2	$P4_2/mnm$; 4.623, 3.052; Mg-a; F-f, 0.31
SiF_4	$I\bar{4}3m$; 5.41; Si-a; F-c, 0.165
βSiO_2 (b)	$P6_222$; 5.02, 5.48; Si-c; O-j, 0.197
$SrBr_2$	Pnma; 11.44, 4.31, 9.22; Sr-c, -0.189, 0.108; Br-c, 0.103, 0.119; Br-c, 0.614, -0.158
$TiCl_2$	$P\bar{3}m1$; 3.561; 5.875; Ti-a; Cl-d, 0.25
TiO_2(rutile)	$P4_2/mnm$; 4.5929, 2.9591; Ti-a; O-f, 0.3056
TiO_2(anatase)	$I4_1/amd$; 3.785, 9.514; Ti-a; O-e, 0.2064
TiO_2(brookite)	Pbca; 9.184, 5.447, 5.145; Ti-c, 0.128, 0.098, 0.863; O-c, 0.008, 0.147, 0.182; O-c, 0.229, 0.110, 0.530

Table I (continued

Compound	Structure
UD_3	Pm3n; 6.64; U-a; U-c; D-k, 0.155, 0.31
V_2O_5	Pmmn; 11.519, 3.564, 4.373; V-f, 0.1486, 0.105; O-f, 0.149, 0.458; O-f, 0.320, 0.000; O-a, 0.000
YCl_3	C2/m; 6.92, 11.94, 6.44, 111.0°; Y-g, 0.166; Cl-i, 0.211, 0.247; Cl-j, 0.229, 0.179, 0.760
YF_3	Pnma; 6.353, 6.850, 4.393; Y-c, 0.3686, 0.0595; F-c, 0.527, 0.577; F-d, 0.180, 0.074, 0.364
Y_2O_3	Ia3; 10.604; Y-b; Y-d, -0.030; O-e, 0.385, 0.145, 0.380
YOCl	P4/nmm; 3.903, 6.597; Y-c, 0.18; O-a; Cl-c, 0.64
ZnO	$P6_3mc$; 3.2495, 5.2069; Zn-b, (0.0); O-b, 0.345
ZnS	$P6_3mc$; 3.819, 6.246; Zn-b, (0.0); S-b, 0.375

(a) Ideal perovskite

(b) High-temperature quartz

Table II. Results of Madelung-constant calculations

Compound	R_0	Correction	$A(R_0)$	β/π	p_c	$\langle R \rangle$	1/m	$\alpha(\langle R \rangle)$
$AlCl_3$	2.2953	0.002	8.303	3	6	2.3165	0.42	1.40
αAl_2O_3	1.8478	0.006	24.242	3	6	1.9174	0.22	1.68
$BeCl_2$	2.0170	0.0011	4.086	3	4	2.0170	0.42	1.36
BeO	1.5987	0.002	6.368	3	4	1.6493	0.25	1.64
BiSCl	2.7226	0.003	10.388	3	4	2.7367	--	--
$CaCl_2$	2.7083	0.0011	4.730	3	6	2.7501	0.28	1.601
CaF_2	2.360352	0.00007	5.03879	5	8	2.360352	0.21	1.68
$CaTiO_3$	1.92000	0.0004	24.7550	5	6	1.92000	--	--
$CdCl_2$	2.6633	0.0011	4.489	3	6	2.6633	0.28	1.50
CdI_2 (Bozorth)	2.988222	0.00007	4.38190	5	6	2.988222	0.28	1.46
CdI_2 (Hassel)	2.988222	0.00007	4.38409	5	6	2.988222	0.28	1.46
CsCl	3.570623	0.00002	1.76268	5	8	3.570623	0.13	1.76
Cu_2O	1.841170	0.00007	4.44249	5	2	1.841170	0.42	1.48
$LaCl_3$	2.9503	0.002	9.129	3	9	2.9801	0.28	1.54
LaF_3	2.3533	0.002	9.119	3	5	2.3782	0.63	1.54
					11	2.5735	0.23	1.66
La_2O_3	2.3711	0.006	24.179	3	4	2.3913	0.25	1.63
LaOCl	2.3964	0.003	10.923	3	4	2.3964	--	--
βLaOF	2.4194	0.003	11.471	3	8	2.5038	--	--
γLaOF	2.42141	0.0002	11.3914	5	8	2.51619	--	--
$MgAl_2O_4$	1.9173	0.007	31.475	3	4	1.9173	--	--

Table II continued

Compound	R_0	Correction	$A(R_0)$	β/π	p_c	$\langle R \rangle$	1/m	$\alpha(\langle R \rangle)$
MgF_2	1.9677	0.0011	4.762	3	6	1.9874	0.28	1.60
NaCl	2.813840	0.00002	1.74756	5	6	2.813840	0.17	1.75
βSiO_2	1.6191	0.004	17.609	3	4	1.6191	0.42	1.47
SiF_4	1.5461	0.004	12.489	3	4	1.5461	0.85	1.25
$SrBr_2$	3.1605	0.0011	4.624	3	7	3.2544	0.24	1.59
$TiCl_2$	2.5267	0.0011	4.347	3	6	2.5267	0.28	1.45
TiO_2 (anatase)	1.93743	0.0003	19.0691	5	6	1.94618	0.28	1.60
TiO_2 (brookite)	1.8424	0.004	18.066	3	6	1.9595	0.28	1.60
TiO_2 (rutile)	1.94511	0.0003	19.0803	5	6	1.95840	0.28	1.60
UD_3	2.0584	0.002	8.728	3	12	2.3252	0.21	1.64
V_2O_5	1.5437	0.01	44.32	3	5	1.8188	0.51	1.49
YCl_3	2.5845	0.002	8.313	3	6	2.6365	0.42	1.41
YF_3	2.1630	0.002	8.899	3	9	2.3213	0.28	1.59
Y_2O_3	2.2532	0.006	24.844	3	6	2.2741	0.22	1.67
YOCl	2.2844	0.003	10.916	3	4	2.2844	--	--
ZnO	1.796380	0.00009	5.99413	5	4	1.980843	0.25	1.65
ZnS (cubic)	2.340867	0.00009	6.55222	5	4	2.340867	0.25	1.64
ZnS (hexagonal)	2.339051	0.00009	6.56292	5	4	2.339850	0.25	1.64

The last two columns in Table II prove useful in checking against blunders in computation. Templeton has observed that the reduced Madelung constant,

$$\alpha(R_0) = 2A(R_0)/z_a z_c n,$$

for several binary salt structures is approximately

$$\alpha = 1.89 - 1/m,$$

where m, the weighted-harmonic-mean coordination number, is defined as

$$1/m = (\Sigma n_i/p_i)/(\Sigma n_i).$$ [9]

In these relations, R_0 is the nearest-neighbor distance, z_a and z_c are the charge numbers of the anion and cation, respectively, n is the number of atoms per formula unit, and n_i is the number of atoms of one kind with coordination number p_i. For structures with several nearest neighbors at slightly different distances, it is perhaps more useful to consider a reduced Madelung constant derived from $A(\langle R \rangle)$ rather than from $A(R_0)$. In Fig. 1 are plotted points corresponding to the $\alpha(\langle R \rangle)$ and 1/m values listed in Table II. The new values fall on or below the previously derived empirical line except for SiF_4, V_2O_5, and LaF_3--three structures which involve some of the atoms in one-fold coordination. This coordination number was not encountered in the previous study, and the correlation is not accurate in such cases. The LaF_3 case is ambiguous in that La has one neighbor at 2.35 A, four at 2.39 A, and six others at 2.74 A. The correlation fails if only the five shortest distances are considered but agrees well if all eleven are included. Only the former case corresponds to one-fold coordination for some of the fluorine atoms.

It is interesting that the reduced Madelung constant for an isolated tetrahedral SiF_4 molecule is 1.23, compared with 1.25 for the crystal; the crystal, therefore, has hardly any coulomb contribution to its molecular cohesion.

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Figure Legend

Fig. 1. Plot of the reduced Madelung constant, $a(\langle R \rangle)$ versus the reciprocal of the weighted-harmonic-mean coordination number, m. The lettered points are (a) V_2O_5, (b) LaF_3 considering only five nearest neighbors in the calculation of $\langle R \rangle$, and (c) SiF_4. The straight line is given by $a = 1.89 - 1/m$.

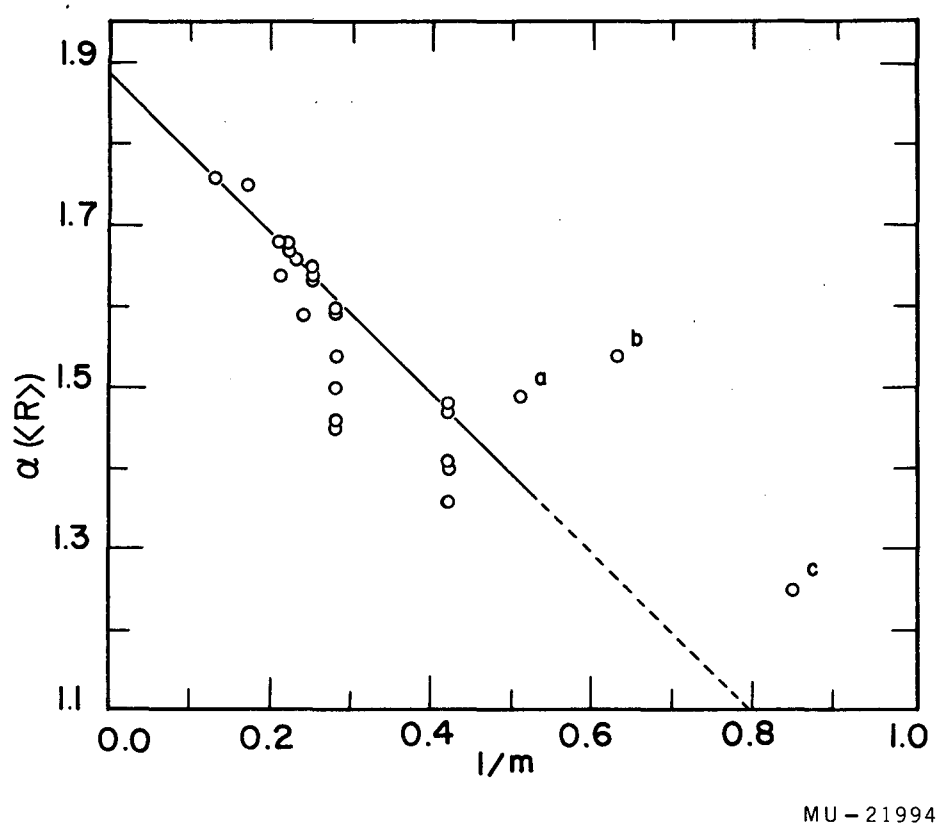

Fig. 1.