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Structure characterization and predictability by Voronoi analysis

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Abstract

The unique ability of tessellation methods to characterize atomic structures is highlighted, with the Voronoi tessellation, by virtue of its freedom from constraining assumptions, emphasized as pre-eminent among these methods. It is demonstrated how to extract information from an atomic structure by constructing its Voronoi tessellation and analysing the results. In so doing, insight is gained into the coordination patterns of the atoms and how their positions are influenced by neighbours. As an example of such a procedure, typical Voronoi volumes are calculated for 72 atom types found in a set of 249 binary intermetallic and ionic compounds. Whereas the various atom types have broadly characteristic volumes, these are also sensitive to the other atom types with which they are combined in a given compound, *i.e.* whether the latter behaves as a metal, semimetal, semiconductor or insulator. Further, smaller variations in volume occur for different atom types within these four categories. Thus, structural information obtained from the Voronoi tessellation may possibly be correlated directly with atomic properties.

1. Introduction

1.1. *Structural characterization and predictability*

When large numbers of atoms are brought together to form crystalline solids, they arrange themselves in particular structures of varying complexity. Although names have been given to all structural types, recognizing that many different combinations of atom types give rise to the same structural topologies, it is still very difficult to predict the structures that an arbitrary given compound will adopt in the solid state.

Two fundamentally different approaches to this problem may be advocated: (i) the quantum-mechanical method of calculating structure from first principles, and (ii) empirical rationalizations utilizing equilibrium atomic positions as primary data. Whereas the first of these describes a structure as a continuous entity (a probability field) in a continuous space, the second method regards structures as discrete entities (typically spheres, either hard or soft) in a continuous space (molecular dynamics and Monte Carlo simulations, sphere-packing models) or in a discrete space (tessellation models).

Although quantum-mechanical simulations, in their simplest form, are straightforward to perform, they are notorious for not being generally applicable and they tend to require quite complex parameters (*e.g.* four-body potentials) to yield reasonable results. Similarly, sphere-packing models have been quite successful, but are of limited applicability.

Tessellation models, by comparison, have not been utilized for predictive purposes to a great extent; moreover, the focus has remained on characterizing the structures observed. However, it is certainly within the scope of such models to answer the most basic question concerning the arrangement of atoms in solids: 'what are the atoms trying to do?' In this connection, it should be pointed out that, although the intrinsic atomic properties are likely to be very complicated (as evidenced by quantum mechanics), the structures observed in nature appear to be finitely variable, with certain structural topologies being adopted by very many different compounds. Thus it is reasonable to start with the structures themselves and to relate the systematic information contained therein to the sets of different atom types adopting the various structures, which are also finite. Tessellation methods may turn out to be pre-eminently suited to this particular task.

Based on a tessellation which wraps each atomic equilibrium position in its own polyhedron, the environment of the atom associated with that polyhedron can be quantified in many ways, for example: (i) polyhedral volume, representing the amount of space the atom requires for itself; (ii) number of faces of the polyhedron, representing atomic coordination number; (iii) number of vertices, which correspond to the voids surrounding the atom; (iv) number of vertices per polyhedral face. Thus, all features of a structure may be quantified. The important question is not whether these quantities have intuitive interpretations, but rather whether their values are sensitive to which atom types are involved. If, for example, having studied many different solids containing carbon it becomes apparent

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that carbon atoms always assume a near-constant value with respect to a particular parameter, then that value of the parameter is a likely natural constant for carbon.† Natural constants of this kind could be sought not only for individual atom types, but also for groups of atoms, *e.g.* molecular fragments or clusters.

The potential benefits of finding such constants are twofold. On the one hand, a more detailed understanding would be obtained of the nature of chemical interactions; on the other, a new kind of simulation would be possible, not based on a prescribed theory of interatomic forces, but rather on naturally occurring structural constants. It should be recognized, however, that if the structures that occur in nature depend strongly on dynamic atomistic properties, any tessellation approach relying solely on static data will probably meet with limited success.

1.2. *Choice of tessellation*

Although the idea of examining the structures of crystals from a geometrical viewpoint has been popular for a long time, with the Voronoi tessellation generally chosen as the starting point for such studies [*cf.* the historical perspective given by Thomas (1996)], the method has never received wide acclaim as a tool for characterizing structure in unaltered form. The principal argument against it is that ionic (or, where appropriate, covalent, metallic or van der Waals) radii are not taken into consideration if the tessellation is constructed by means of bisecting planes between the atomic centres. Clearly, situations will arise in which either the Voronoi polyhedra do not enclose the atoms (represented by spheres) fully or the polyhedra are much larger than the spherical atoms enclosed. In order to remedy this apparent problem, various alterations to the basic Voronoi tessellation have been proposed. Hoppe (1970) introduced a principle whereby the dividing planes were positioned, not midway between the centres of neighbouring atoms, but at distances from the atom centres in proportion to the two relevant radii. However, the inclusion of atomic radii comes at a cost, since the space-filling property may no longer generally be assumed, with parts of space not assigned to any particular atom. By comparison, the approach of radical planes (Fischer *et al.*, 1971), in which all points in the dividing planes are equidistant from the tangent points on both spheres, ensures space filling. However, it suffers from having no simple intuitive interpretation. A more elaborate method of preserving space filling, which has recently been employed by Goede *et al.* (1997), relaxes the constraint that the Voronoi polyhedra have plane faces. According to this, the faces are allowed to be hyperbolic planes positioned such that all points in the planes are equidistant from the spherical atomic surfaces. Moreover, every point inside a given polyhedron is closer to the sphere contained in the polyhedron than to any other sphere.

Despite the appeal of taking atomic radii into consideration, all these latter methods quantify structure *overlaid by chemical assumptions*. By comparison, the original Voronoi tessellation is a means of quantifying pure structure. In this basic method, the source data required to calculate the tessellations are the points corresponding to the equilibrium positions of the atomic nuclei, as generally determined experimentally by X-ray or neutron diffraction. In essence, information that is conventionally conveyed by atomic radii is encoded in the tessellation itself.‡ Thus, the search for links between atomic properties and structure can be carried out without making *a priori* chemical assumptions.

2. Methods and systems

This study is an effort to widen the applicability of structural analyses based on the Voronoi tessellation, following earlier work by Thomas (1996) in which the method of performing the Voronoi tessellation has been described. It may also be regarded as a natural extension of much earlier work by Mackay (1972). In essence, the form of a given Voronoi polyhedron is indicative of *the response of the atom at its centre to its atomic environment*.

Owing to wide variations in crystal symmetry between different chemical systems, it is not straightforward to specify *a priori* how many parameters will be needed to define the corresponding Voronoi polyhedra unambiguously. In general, however, it is desirable to limit the number of parameters used, such that size and shape are adequately described. Examples of possible polyhedral descriptors are enclosed volumes, numbers of corners, edges and faces, average facial areas and distances, together with derived topological quantities such as face-interaction indices (Thomas, 1996), which are of chemical significance.

As a starting point, this article deals solely with polyhedral volumes, in order to demonstrate the principles of carrying out a systematic structural analysis by means of the Voronoi tessellation. Such volumes also have a direct intuitive interpretation, unlike other, derived, parameters. The structures chosen for the study correspond to a set of 249 binary inorganic compounds of stoichiometries ranging from AB to AB_{13} (Table 1). These span all common structural types; they were selected by Pettifor (1986) in an earlier systematic study,

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† The expression ‘natural constant’ is here chosen for lack of a better expression; in reality, the value cannot be expected to be truly constant, only approximately so.

‡ The atomic/ionic radii are derived from numerous measurements of interatomic distances between near neighbours and, in fact, this distance is a very appropriate structural parameter to include in a Voronoi-tessellation analysis. Atomic/ionic radii may therefore be calculated from a suitable array of Voronoi-tessellated structures.

Table 1. *Systems analysed in this study (average volumes in* $\AA^3$*)*

System	1	$\langle V_1 \rangle$	2	$\langle V_2 \rangle$	System	1	$\langle V_1 \rangle$	2	$\langle V_2 \rangle$	System	1	$\langle V_1 \rangle$	2	$\langle V_2 \rangle$
Ag_2O	Ag	19.45	O	13.79	CdSb	Cd	29.25	Sb	27.61	HoD_3	H	9.72	Ho	8.51
Ag_2Te	Ag	22.36	Te	23.11	$CeCu_2$	Cu	18.20	Ce	21.96	$HoSb_2$	Ho	25.80	Sb	25.04
$Al_{12}W$	Al	16.98	W	14.06	$CeCu_6$	Cu	14.36	Ce	18.88	$IrSe_2$	Ir	15.38	Se	21.40
Al_2Cu	Cu	12.62	Al	16.13	Co_2Al_5	Al	14.55	Co	12.10	IrV	Ir	13.74	V	13.60
Al_2O_3	Al	7.14	O	9.37	Co_2Si	Co	11.03	Si	10.60	La_2O_3	La	15.11	O	17.40
Al_2Zr_3	Al	18.41	Zr	21.67	$CoAs_3$	Co	12.90	As	18.63	La_2Sb	La	33.26	Sb	30.40
Al_3Os_2	Al	13.86	Os	13.42	$CoGa_3$	Co	11.68	Ga	17.27	LaF_3	La	12.06	F	14.20
Al_3Ti	Al	15.89	Ti	15.89	CoO	Co	9.58	O	9.58	Li_2Sb	Li	20.30	Sb	18.90
Al_3Zr	Al	17.29	Zr	17.45	$CoSb_2$	Co	16.41	Sb	21.91	LiAs	Li	19.36	As	16.70
Al_3Zr_2	Al	17.73	Zr	19.92	CoSn	Co	14.30	Sn	19.94	$MgCu_2$	Cu	13.35	Mg	16.40
Al_4Ba	Al	21.24	Ba	29.99	Cr_2S_3	Cr	13.79	S	19.08	$MgNi_2$	Ni	12.35	Mg	15.20
Al_4U	Al	19.04	U	18.62	Cr_3C_2	Cr	9.39	C	8.35	$MgZn_2$	Mg	19.21	Zn	15.70
Al_4W	Al	16.41	W	14.54	Cr_3Si	Cr	11.98	Si	11.61	Mn_2O_3	Mn	9.02	O	11.30
Al_5W	Al	15.36	W	15.36	Cr_5B_3	Cr	9.82	B	8.11	Mn_4B	Mn	10.08	B	7.72
Al_6Mn	Al	16.03	Mn	12.71	CrB	Cr	9.74	B	7.36	Mn_5C_2	Mn	10.33	C	7.97
AlB_2	Al	10.33	B	7.57	$CrSi_2$	Cr	12.02	Si	12.03	MnP	Mn	12.02	P	12.60
AlCe	Al	23.12	Ce	28.13	CS_2	C	19.65	S	29.59	MnU_6	Mn	15.49	U	20.50
$AlCl_3$	Al	12.41	Cl	25.31	CsCl	Cs	34.84	Cl	34.84	Mo_2B_5	Mo	10.14	B	6.90
AlCu	Cu	12.87	Al	15.19	CsO	Cs	31.19	O	21.04	Mo_2S_3	Mo	14.06	S	18.10
AlDy	Al	20.55	Dy	25.71	Cu_2Sb	Cu	15.28	Sb	18.27	MoB	Mo	12.01	B	8.48
As_2Ge	As	24.57	Ge	20.75	Cu_3Au	Cu	13.23	Au	13.23	MoC	Mo	9.73	C	9.45
As_2S_3	As	20.79	S	25.11	Cu_3P	Cu	12.96	P	11.04	MoF_5	Mo	6.35	F	16.30
$AsBr_3$	As	24.90	Br	36.78	Cu_3Ti	Cu	12.71	Ti	12.71	$MoNi_4$	Ni	11.66	Mo	11.70
AsGe	As	40.24	Ge	40.24	$CuCl_2$	Cu	15.25	Cl	25.27	$MoPt_2$	Mo	14.44	Pt	14.90
AsO	As	22.95	O	27.04	$CuMg_2$	Cu	14.94	Mg	19.86	MoS_2	Mo	13.74	S	19.80
AsTi	Ti	17.43	As	17.99	CuP_2	Cu	16.99	P	15.70	$MoSi_2$	Mo	13.45	Si	13.40
Au_2V	Au	15.87	V	16.04	CuTi	Cu	13.29	Ti	15.28	Na_3As	Na	26.34	As	22.30
Au_4Zr	Au	17.33	Zr	17.33	$CuTi_3$	Cu	15.53	Ti	15.53	NaCl	Na	22.19	Cl	22.20
$AuBe_5$	Au	10.79	Be	9.17	Fe_2C	Fe	10.76	C	7.21	NaO	Na	14.24	O	10.60
AuCd	Au	18.31	Cd	18.30	Fe_2N	Fe	10.96	N	7.31	NaP	Na	24.76	P	18.40
AuCu	Cu	14.42	Au	14.42	Fe_2P	Fe	11.95	P	10.47	NaPb	Na	33.22	Pb	28.90
$BaCd_{11}$	Ba	34.70	Cd	22.26	Fe_3C	Fe	10.39	C	7.67	NaTl	Na	25.97	Tl	25.97
$BaHg_{11}$	Ba	32.74	Hg	23.83	FeB	Fe	9.27	B	7.14	NbAs	Nb	17.40	As	17.40
$BaPb_3$	Ba	32.95	Pb	32.91	$FeCl_3$	Fe	13.48	Cl	26.34	$NbCl_5$	Nb	13.24	Cl	29.40
BaS_2	Ba	29.53	S	28.79	FeS_2*m*	Fe	11.40	S	14.60	NbI_4	Nb	20.70	I	39.00
$BaSi_2$	Ba	34.37	Si	26.72	FeS_2*p*	Fe	11.69	S	14.04	NbS_2	Nb	14.34	S	21.03
$BaZn_5$	Ba	29.73	Zn	18.26	$FeSb_2$	Fe	16.87	Sb	22.05	$NbSb_2$	Nb	19.85	Sb	23.60
BCl_3	B	15.08	Cl	29.92	FeSi	Fe	11.25	Si	11.37	$NbSe_3$	Nb	16.18	Se	23.01
$Be_{12}Mo$	Be	8.37	Mo	11.47	$FeSi_2$	Fe	10.29	Si	13.32	$NbTe_2$	Nb	20.66	Te	28.96
Be_3Nb	Be	9.74	Nb	12.90	Ga_2Mg_5	Ga	18.98	Mg	21.36	$NbTe_4$	Nb	19.97	Te	31.70
Bi_2Te_3	Bi	30.88	Te	35.97	Ga_2S_3	Ga	18.54	S	23.46	Nd_2Te_5	Nd	28.40	Te	31.50
BiF_3	Bi	12.53	F	12.53	GaMg	Ga	17.86	Mg	20.47	$NdAs_2$	Nd	23.91	As	23.10
BiSe	Bi	27.89	Se	29.61	GaS	Ga	19.61	S	23.59	$NdTe_3$	Nd	27.67	Te	31.50
CaB_6	Ca	18.85	B	8.73	GaTe	Ga	25.84	Te	34.04	Ni_2Al_3	Ni	12.06	Al	14.90
CaC_2	Ca	17.46	C	15.24	Gd_2S_3	Gd	20.54	S	23.12	Ni_2In	Ni	13.06	in	12.80
$CaCl_2$	Ca	20.92	Cl	31.67	Ge_3Rh_5	Rh	14.07	Ge	13.46	Ni_3P	Ni	11.50	P	9.45
$CaCu_5$	Cu	14.15	Ca	20.09	GeK	K	38.13	Ge	27.10	Ni_3S_2	Ni	13.24	S	13.90
CaF_2	Ca	11.40	F	14.57	$GePt_3$	Pt	15.12	Ge	14.44	Ni_3Sn	Ni	12.84	Sn	12.80
$CaIn_2$	Ca	28.83	in	25.79	GeS	Ge	20.17	S	20.79	Ni_3Ti	Ni	11.70	Ti	11.70
$CaSb_2$	Ca	29.59	Sb	28.42	$HfGa_2$	Ga	8.62	Hf	8.79	NiS	Ni	13.02	S	15.03
$CaSi_2$	Ca	25.66	Si	19.99	Hg_4Pt	Hg	25.60	Pt	16.76	$OsGe_2$	Os	14.10	Ge	16.30
Cd_2Ce	Cd	25.29	Ce	26.31	Hg_5Mn_2	Hg	21.16	Mn	18.48	OsO_4	Os	8.85	O	18.20
Cd_6Y	Cd	19.49	Y	24.70	HgMn	Hg	17.91	Mn	17.91	PbO	Pb	21.21	O	16.95
$CdCl_2$	Cd	20.14	Cl	27.34	HgO	Hg	16.13	O	16.02	PbO_2	Pb	10.46	O	15.00
CdI_2	Cd	26.67	I	40.16	HgS	Hg	12.01	S	11.54	Pd_2As	Pd	14.90	As	13.90
Pd_4Se	Pd	16.13	Se	12.78	SF_6	S	3.86	F	28.97	TiO_2bro	Ti	7.65	O	12.20
$PdCl_2$	Pd	19.07	Cl	25.46	Si_2U_3	U	22.62	Si	18.45	TiO_2ii	Ti	7.67	O	11.50
PdF_3	Pd	8.53	F	14.19	SiS_2	Si	15.94	S	28.89	TiO_2rut	Ti	7.57	O	11.80
PdS	Pd	17.49	S	16.78	SiU_3	U	19.73	Si	19.89	$TiSi_2$	Ti	14.20	Si	14.10
$PdSe_2$	Pd	19.04	Se	22.29	$SmSb_2$	Sm	27.58	Sb	27.96	U_3S_5	U	20.42	S	23.10
PH_3	H	13.79	P	21.45	$SnBr_4$	Sn	22.73	Br	43.01	UCl_3	U	19.88	Cl	27.96
Pt_2Ga	Ga	14.59	Pt	14.82	SnF_4	Sn	7.71	F	14.33	UF_4	U	9.96	F	16.90
$PtHg_2$	Hg	23.60	Pt	16.79	SnI_4	Sn	31.54	I	49.70	UF_5	U	9.13	F	17.20
PtS	Pt	18.62	S	18.10	$SrBr_2$	Sr	27.39	Br	34.42	UF_6	U	7.16	F	18.10
$PtSn_4$	Pt	18.12	Sn	24.71	SrI_2	Sr	34.53	I	44.51	V_2N	V	12.01	N	7.85
Pu_2C_3	Pu	15.18	C	12.28	Ta_2O_5	Ta	8.48	O	13.88	V_3S	V	13.37	S	11.20

Table 1 (*cont.*)

System	1	$\langle V_1 \rangle$	2	$\langle V_2 \rangle$
Pu_2S_3	Pu	21.18	S	21.88
$PuBr_3$	Pu	24.18	Br	31.45
$PuGa_6$	Ga	18.45	Pu	23.77
Rb_6O	Rb	73.94	O	21.03
Re_3B	Re	12.97	B	9.93
ReB_2	Re	10.50	B	8.37
ReO_3	Re	6.58	O	15.36
Rh_2S_3	Rh	13.73	S	16.75
Ru_2Si_3	Ru	12.85	Si	14.21
RuB_2	Ru	10.11	B	8.40
$RuCl_3$	Ru	12.93	Cl	26.30
RuF_5	Ru	7.42	F	14.53
Sb_2S_3	Sb	22.09	S	25.88
$SbCl_5$	Sb	15.85	Cl	35.75
Sc_2S_3	Sc	16.30	S	24.48
Se_3U	U	21.29	Se	29.15
SeTl	Tl	27.83	Se	28.78
Ta_2P	Ta	16.44	P	14.29
$TeCl_4$	Te	17.58	Cl	33.39
Th_2S_5	Th	19.54	S	21.86
ThB_4	Th	16.78	B	9.34
ThC_2	Th	16.50	C	14.95
$ThCl_4$	Th	18.62	Cl	29.06
ThH_2	H	14.53	Th	11.80
$ThMn_{12}$	Mn	14.05	Th	20.46
$ThSi_2$	Th	23.87	Si	18.60
Ti_2Ni	Ni	13.46	Ti	15.93
Ti_2Pd_3	Pd	15.39	Ti	15.24
Ti_3P	Ti	14.13	P	19.43
Ti_3Pd_5	Pd	15.22	Ti	15.22
Ti_3Pt_5	Pt	15.28	Ti	15.10
$TiCl_3$	Ti	14.21	Cl	27.32
TiI_3	Ti	20.40	I	41.13
TiO_2ana	Ti	7.62	O	13.22
VF_3	V	7.25	F	14.90
VF_5	V	5.61	F	15.90
VO_2	V	7.27	O	11.20
W_2B_5	W	9.93	B	6.71
W_5Si_3	W	14.89	Si	13.70
WC	W	10.37	C	10.40
WCl_6	W	11.72	Cl	28.40
YF_3	Y	9.88	F	12.70
YZn_3	Y	21.49	Zn	17.70
Zn_3P_2	Zn	20.22	P	16.60
ZnP_2	Zn	21.58	P	19.20
ZrF_4	Zr	7.83	F	13.10
$ZrGa_2$	Ga	17.60	Zr	17.90
ZrO_2	Zr	9.31	O	12.80
$ZrSb_2$	Zr	21.96	Sb	25.20
$ZrSe_3$	Zr	17.97	Se	25.70
$ZrSi_2$	Zr	16.98	Si	16.70

which was not concerned with the Voronoi tessellation. However, this choice of chemical systems is arbitrary, since the Voronoi tessellation and subsequent analysis can be applied to all solids, irrespective of prevalent bonding type.

3. Results

The Voronoi tessellation was carried out on all 249 binary systems, as described above. The calculated polyhedral volumes, always taken as mean values† for both atom types within a particular structure, are presented below, according to four alternative conventions.

3.1. *Global mean polyhedral volume*

The mean volume enclosed by a Voronoi polyhedron, regardless of atom type, has been found to be 18.1 Å^3. (No calculations of Voronoi polyhedra are needed to obtain this value since it is simply the unit-cell volume divided by the number of atoms.)

3.2. *Mean polyhedral volume for each atom type*

The 249 systems give rise to polyhedral volumes for the 72 distinct atom types as listed in Table 2. Two points should be noted: (i) no account has been taken of the other atom type in the binary compounds; (ii) the size of the data set is relatively small, there being many other known structures of binary compounds involving the 72 atom types listed.

3.3. *Mean polyhedral volumes for each atom type, classified according to the characters of the other atoms with which they are combined*

Mean volumes for the 72 atom types are subdivided further in Table 2, according to whether the other atom types with which they are combined behave as metals, semimetals, semiconductors or insulators in elemental form.

3.4. *Mean polyhedral volumes for each atom type, classified according to the individual identities of the other atoms with which they are combined*

This is the highest level of definition, with averages taken, where possible, over different chemical compositions for each unique pair of atom types. This analysis is indicative, rather than comprehensive, since many more structural data are available than have been analysed here. In summary, 210 different pairs of atom types have been identified, yielding 420 mean polyhedral volumes (Table 3).

3.5. *Quantitative comparison of the results in §§3.1 to 3.4*

For each of the four methods described for calculating mean polyhedral volumes, designated 1 to 4 (§§3.1 to 3.4, respectively), deviations from these means may be defined as follows for all atom types and structures:

$$E = |V_{x,\text{observed}} - V_{x,k}|/V_{x,\text{observed}}.$$

Here x stands for A or B (in A_mB_n compounds), k is the method number, $V_{x,\text{observed}}$ is an observed polyhedral volume and $V_{x,k}$ is the average polyhedral volume for atom type x according to method k.

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† This is a raw mean value over all atoms of the particular type in the entire unit cell, not merely those in the asymmetric unit. Moreover, all atoms are given equal weight. It could here be argued that this procedure overemphasizes the importance of atoms with many congruent (or inversely congruent) polyhedra over those with only a few (or none). However, the focus here is entirely on solids and the fraction of space in these devoted to each atom type. By taking raw mean values we gain knowledge about the space requirements of each investigated atom type in a solid rather than about the space requirements of each individual atom.

Table 2. *Average polyhedral volumes (Å^3): methods 2 and 3*

m = metal; sm = semimetal; sc = semiconductor; i = insulator; ξ is the number of symmetrically inequivalent atoms included in the average.

Atom type	Method 2		Method 3 in compound with:							
			m		sm		sc		i	
	$\langle V\rangle$	ξ	$\langle V\rangle$	ξ	$\langle V\rangle$	ξ	$\langle V\rangle$	ξ	$\langle V\rangle$	ξ
Ag	20.9	3					22.4	2	19.5	1
Al	16.1	46	17.2	43			10.3	1	9.8	2
As	21.9	23	18.6	11			32.4	5	22.9	7
Au	15.0	11	15.0	11						
B	8.6	23	8.1	22					15.1	1
Ba	32.0	10	32.0	7			34.4	2	29.5	1
Be	9.1	8	9.1	8						
Bi	23.8	5					29.4	4	12.5	1
Br	36.4	13	36.3	10	36.8	3				
C	11.3	12	10.4	11					19.7	1
Ca	21.6	8	24.5	2	29.6	1	22.3	2	16.6	3
Cd	23.1	15	21.3	12	29.3	1			23.4	2
Ce	23.8	4	23.8	4						
Cl	28.6	32	27.6	21	35.8	2	31.7	9		
Co	12.6	9	12.7	4	14.7	2	11.0	2	9.6	1
Cr	11.1	11					10.9	5	11.6	6
Cs	33.0	2							33.0	2
Cu	14.4	27	14.1	19	15.3	2	15.0	5	15.3	1
Dy	25.7	2	25.7	2						
F	15.9	63	15.1	52	12.5	2			29.0	9
Fe	11.7	13			16.9	1	10.7	5	11.5	7
Ga	17.7	20	16.2	14			25.8	3	19.1	3
Gd	20.5	2							20.5	2
Ge	21.8	11	17.8	7	30.5	3			20.2	1
H	12.7	5	12.1	4			13.8	1		
Hf	8.8	1	8.8	1						
Hg	20.0	11	22.4	9					14.1	2
Ho	17.2	2	8.5	1	25.8	1				
I	42.9	12	42.9	12						
In	19.3	2	19.3	2						
Ir	14.6	3	13.7	1			15.4	2		
K	38.1	2					38.1	2		
La	20.1	4			33.3	2			13.6	2
Li	19.8	4			19.8	4				
Mg	18.7	10	18.8	10						
Mn	13.3	15	15.7	7			11.1	3	9.7	5
Mo	11.7	13	12.5	3			11.9	3	11.0	7
N	7.6	4	7.6	4						
Na	24.5	10	29.6	3	26.3	2	24.8	2	18.2	3
Nb	17.2	13	12.9	2	18.6	2	18.9	6	16.1	3
Nd	26.7	4			23.9	1	28.0	3		
Ni	12.5	16	12.5	11			11.5	3	13.1	2
O	14.7	63	14.1	59	27.0	4				
Os	12.1	3	13.4	1			14.1	1	8.9	1
P	15.3	19	15.3	19						
Pb	23.4	5	30.9	3					15.8	2
Pd	15.7	16	15.3	5	14.9	4	17.6	2	15.0	5
Pt	16.3	16	16.1	12			15.1	3	18.6	1
Pu	21.1	4	23.8	1					20.2	3
Rb	73.9	4							73.9	4
Re	10.0	4					11.7	3	6.6	1
Rh	13.9	4					14.1	3	13.7	1
Ru	10.8	8					11.5	5	10.2	3
S	19.8	45	19.1	34	25.5	6	24.8	2	16.7	3
Sb	23.6	22	24.5	19					19.0	3
Sc	16.3	2							16.3	2
Se	24.1	25	23.3	22	29.6	3				
Si	15.7	23	15.7	22					15.9	1
Sm	27.6	1			27.6	1				
Sn	19.9	8	19.2	5					20.7	3
Sr	31.0	3							31.0	3
Ta	12.5	19					16.4	6	8.5	13
Te	29.3	20	30.1	16	36.0	2			17.6	2
Th	18.2	7	16.1	2			20.3	2	18.2	3
Ti	13.5	23	14.7	12	17.4	1	14.2	4	10.9	6
Tl	26.9	3	26.0	1			27.8	2		
U	16.9	15	19.6	3			21.2	5	13.3	7
V	10.7	11	14.8	3					9.1	8
W	13.0	10	14.7	4			12.4	3	11.0	3
Y	18.7	3	23.1	2					9.9	1
Zn	18.7	12	17.2	8			20.9	4		
Zr	16.8	13	18.9	7	22.0	2	17.5	2	8.6	2

A rapid comparison of methods 1 to 4 may be made by taking averages of the deviations occurring in the different methods, as shown in Table 4. A complete listing of the deviations for all atom types and structures has been deposited with the IUCr.†

4. Discussion

In proceeding from method 1 (average polyhedral volume of 18.1 Å^3) to method 2, which yields values from 7.6 (N) to 73.9 Å^3 (Rb), the considerable extent of the variation between different atom types becomes apparent. Going one step further, method 3 indicates how the polyhedral volumes of a given atom type are influenced by the properties of the atoms with which it is combined. In some cases, the volume of a given atom type is extremely variable, whereas, in others, this is not so. Zirconium mean volumes, for example, show wide variations, being 22.0 Å^3 when combined with semimetals, *ca* 18 Å^3 with metals or semiconductors and a mere 8.6 Å^3 with insulators. Palladium, on the other hand, maintains a much more constant volume, ranging from 14.9 Å^3 with a semimetal to 17.6 Å^3 with a semiconductor.

Further diversification within the limited data set analysed is revealed by method 4. For example, carbon polyhedral volumes with metals vary between approximately 8 Å^3 with Cr, Fe and Mn to *ca* 15 Å^3 with Ca and Th. By comparison, the corresponding volume range for Ni is narrower (11.7–13.1 Å^3).

Since the average errors decrease in the order method 1 > method 2 > method 3 > method 4, the essential inference is that the observed variations are not merely random. An improvement in the characteristic volumes for different atom types is observed in proceeding from

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† Supplementary data for this paper are available from the IUCr electronic archives (Reference: AU0167). Services for accessing these data are described at the back of the journal.

Table 3. *Average polyhedral volumes (Å^3): method 4*

Volumes are for the atom type in column 1 when in compound with the atom types in columns 2–12. Numbers in parentheses are numbers of symmetrically inequivalent atoms included in the average.

Ag:	O (1) 19.5	Te (2) 22.4									
Al:	B (1) 10.3	Ba (3) 21.2	Ce (2) 23.1	Cl (1) 12.4	Co (3) 14.6	Cu (4) 15.7	Dy (2) 20.6	Mn (3) 16.0	Ni (2) 14.9	O (1) 7.1	Os (2) 13.9
	Ti (2) 15.9	U (3) 19.0	W (11) 16.3	Zr (6) 17.8							
As:	Br (1) 24.9	Co (1) 18.6	Ge (5) 32.4	Li (2) 16.7	Na (1) 22.3	Nb (1) 17.4	Nd (2) 23.1	O (4) 23.0	Pd (2) 13.9	S (2) 20.8	Ti (2) 18.0
Au:	Be (1) 10.8	Cd (1) 18.3	Cu (3) 13.8	V (2) 15.9	Zr (4) 17.3						
B:	Al (1) 7.6	Ca (1) 8.7	Cl (1) 15.1	Cr (3) 7.7	Fe (1) 7.1	Mn (1) 7.7	Mo (4) 7.7	Re (2) 9.2	Ru (2) 8.4	Th (3) 9.3	W (4) 6.7
Ba:	Al (2) 30.0	Cd (1) 34.7	Hg (1) 32.7	Pb (2) 33.0	S (1) 29.5	Si (2) 34.4	Zn (1) 29.7				
Be:	Au (2) 9.2	Mo (3) 8.4	Nb (3) 9.7								
Bi:	F (1) 12.5	Se (3) 27.9	Te (1) 30.9								
Br:	As (3) 36.8	Pu (2) 31.5	Sn (4) 43.0	Sr (4) 34.4							
C:	Ca (1) 15.2	Cr (2) 8.4	Fe (2) 7.4	Mn (1) 8.0	Mo (2) 9.5	Pu (1) 12.3	S (1) 19.7	Th (1) 15.0	W (1) 10.4		
Ca:	B (1) 18.9	C (1) 17.5	Cl (1) 20.9	Cu (1) 20.1	F (1) 11.4	In (1) 28.8	Sb (1) 29.6	Si (1) 25.7			
Cd:	Au (1) 18.3	Ba (3) 22.3	Ce (1) 25.3	Cl (1) 20.1	I (1) 26.7	Sb (1) 29.3	Y (7) 19.5				
Ce:	Al (1) 28.1	Cd (1) 26.3	Cu (2) 20.4								
Cl:	Al (2) 25.3	B (1) 29.9	Ca (1) 31.7	Cd (1) 27.3	Cs (1) 34.8	Cu (1) 25.3	Fe (1) 26.3	Na (1) 22.2	Nb (5) 29.4	Pd (1) 25.5	Ru (1) 26.3
	Sb (2) 35.8	Te (8) 33.4	Th (1) 29.1	Ti (1) 27.3	U (1) 28.0	W (3) 28.4					
Co:	Al (2) 12.1	As (1) 12.9	Ga (1) 11.7	O (1) 9.6	Sb (1) 16.4	Si (2) 11.0	Sn (1) 14.3				
Cr:	B (3) 9.8	C (3) 9.4	S (3) 13.8	Si (2) 12.0							
Cs:	Cl (1) 34.8	O (1) 31.2									
Cu:	Al (4) 12.7	Au (2) 13.8	Ca (2) 14.2	Ce (6) 16.3	Cl (1) 15.3	Mg (2) 14.1	P (5) 15.0	Sb (2) 15.3	Ti (3) 13.8		
Dy:	Al (2) 25.7										
F:	Bi (2) 12.5	Ca (1) 14.6	La (3) 14.2	Mo (6) 16.3	Pd (1) 14.2	Ru (10) 14.5	S (9) 29.0	Sn (2) 14.3	U (13) 17.4	V (8) 15.4	Y (2) 12.7
	Zr (6) 13.1										
Fe:	B (1) 9.3	C (3) 10.6	Cl (1) 13.5	N (1) 11.0	P (2) 12.0	S (2) 11.5	Sb (1) 16.9	Si (2) 10.8			
Ga:	Co (2) 17.3	Hf (2) 8.6	Mg (2) 18.4	Pt (3) 14.6	Pu (2) 18.5	S (3) 19.1	Te (3) 25.8	Zr (3) 17.6			
Gd:	S (2) 20.5										
Ge:	As (3) 30.5	K (2) 27.1	Os (2) 16.3	Pt (1) 14.4	Rh (2) 13.5	S (1) 20.2					
H:	Ho (3) 9.7	P (1) 13.8	Th (1) 14.5								
Hf:	Ga (1) 8.8										
Hg:	Ba (4) 23.8	Mn (3) 19.5	O (1) 16.1	Pt (2) 24.6	S (1) 12.0						
Ho:	H (1) 8.5	Sb (1) 25.8									
I:	Cd (1) 40.2	Nb (6) 39.0	Sn (2) 49.7	Sr (2) 44.5	Ti (1) 41.1						

Table 3 (*cont.*)

In:	Ca (1)	Ni (1)									
	25.8	12.8									
Ir:	Se (2)	V (1)									
	15.4	13.7									
K:	Ge (2)										
	38.1										
La:	F (1)	O (1)	Sb (2)								
	12.1	15.1	33.3								
Li:	As (2)	Sb (2)									
	19.4	20.3									
Mg:	Cu (3)	Ga (4)	Ni (2)	Zn (1)							
	18.1	20.9	15.2	19.2							
Mn:	Al (1)	B (2)	C (3)	Hg (2)	O (2)	P (1)	Th (3)	U (1)			
	12.7	10.1	10.3	18.2	9.0	12.0	14.1	15.5			
Mo:	B (2)	Be (1)	C (2)	F (2)	Ni (1)	Pt (1)	S (3)	Si (1)			
	11.1	11.5	9.7	6.4	11.7	14.4	13.9	13.5			
N:	Fe (2)	V (2)									
	7.3	7.9									
Na:	As (2)	Cl (1)	O (2)	P (2)	Pb (2)	Tl (1)					
	26.3	22.2	14.2	24.8	33.2	26.0					
Nb:	As (1)	Be (2)	Cl (1)	I (1)	S (1)	Sb (1)	Se (3)	Te (3)			
	17.4	12.9	13.2	20.7	14.3	19.9	16.2	20.3			
Nd:	As (1)	Te (3)									
	23.9	28.0									
Ni:	Al (1)	In (2)	Mg (3)	Mo (1)	P (3)	S (2)	Sn (1)	Ti (3)			
	12.1	13.1	12.4	11.7	11.5	13.1	12.8	12.6			
O:	Ag (1)	Al (1)	As (4)	Co (1)	Cs (1)	Hg (1)	La (2)	Mn (1)	Na (2)	Os (2)	Pb (2)
	13.8	9.4	27.0	9.6	21.0	16.0	17.4	11.3	10.6	18.2	16.0
	Rb (1)	Re (1)	Ta (34)	Ti (5)	V (2)	Zr (2)					
	21.0	15.4	13.9	12.2	11.2	12.8					
Os:	Al (1)	Ge (1)	O (1)								
	13.4	14.1	8.9								
P:	Cu (3)	Fe (2)	H (1)	Mn (1)	Na (2)	Ni (1)	Ta (3)	Ti (1)	Zn (5)		
	13.4	10.5	21.5	12.6	18.4	9.5	14.3	19.4	17.9		
Pb:	Ba (2)	Na (1)	O (2)								
	32.9	28.9	15.8								
Pd:	As (4)	Cl (1)	F (1)	S (3)	Se (2)	Ti (5)					
	14.9	19.1	8.5	17.5	17.6	15.3					
Pt:	Ga (5)	Ge (3)	Hg (2)	Mo (1)	S (1)	Sn (1)	Ti (3)				
	14.8	15.1	16.8	14.9	18.6	18.1	15.3				
Pu:	Br (1)	C (1)	Ga (1)	S (1)							
	24.2	15.2	23.8	21.2							
Rb:	O (4)										
	73.9										
Re:	B (3)	O (1)									
	11.7	6.6									
Rh:	Ge (3)	S (1)									
	14.1	13.7									
Ru:	B (2)	Cl (1)	F (2)	Si (3)							
	10.1	12.9	7.4	12.9							
S:	As (3)	Ba (1)	C (1)	Cr (1)	F (2)	Fe (2)	Ga (4)	Gd (3)	Ge (1)	Hg (1)	Mo (4)
	25.1	28.8	29.6	19.1	3.9	14.3	23.5	23.1	20.8	11.5	18.9
	Nb (1)	Ni (1)	Pd (1)	Pt (1)	Pu (1)	Rh (2)	Sb (3)	Sc (2)	Si (1)	Th (3)	U (4)
	21.0	14.5	16.8	18.1	21.9	16.8	25.9	24.5	28.9	21.9	23.1
	V (1)										
	11.2										
Sb:	Ca (2)	Cd (1)	Cl (1)	Co (2)	Cu (1)	Fe (1)	Ho (1)	La (1)	Li (2)	Nb (2)	S (2)
	28.4	27.6	15.9	21.9	18.3	22.1	25.0	30.4	18.9	23.6	22.1
	Sm (2)	Zr (4)									
	28.0	25.2									
Sc:	S (2)										
	16.3										
Se:	Bi (3)	Ir (4)	Nb (9)	Pd (2)	Tl (1)	U (3)	Zr (3)				
	29.6	21.4	23.0	17.5	28.8	29.2	25.7				

Table 3 (*cont.*)

Si:	Ba (3)	Ca (2)	Co (1)	Cr (2)	Fe (2)	Mo (1)	Ru (3)	S (1)	Th (1)	Ti (1)	U (2)
	26.7	20.0	10.6	11.8	12.3	13.4	14.2	15.9	18.6	14.1	19.2
	W (2)	Zr (2)									
	13.7	16.7									
Sm:	Sb (1)										
	27.6										
Sn:	Br (1)	Co (2)	F (1)	I (1)	Ni (1)	Pt (2)					
	22.7	19.9	7.7	31.5	12.8	24.7					
Sr:	Br (2)	I (1)									
	27.4	34.5									
Ta:	O (13)	P (6)									
	8.5	16.4									
Te:	Ag (1)	Bi (2)	Cl (2)	Ga (3)	Nb (4)	Nd (8)					
	23.1	36.0	17.6	34.0	30.4	31.5					
Th:	B (1)	C (1)	Cl (1)	H (1)	Mn (1)	S (1)	Si (1)				
	16.8	16.5	18.6	11.8	20.5	19.5	23.9				
Ti:	Al (1)	As (1)	Cl (1)	Cu (2)	I (1)	Ni (4)	O (4)	P (3)	Pd (3)	Pt (2)	Si (1)
	15.9	17.4	14.2	14.5	20.4	13.8	7.6	14.1	15.2	15.1	14.2
Tl:	Na (1)	Se (2)									
	26.0	27.8									
U:	Al (1)	Cl (1)	F (4)	Mn (2)	S (2)	Se (1)	Si (4)				
	18.6	19.9	8.8	20.5	20.4	21.3	21.2				
V:	Au (2)	F (3)	Ir (1)	N (1)	O (1)	S (3)					
	16.0	6.4	13.6	12.0	7.3	13.4					
W:	Al (4)	B (1)	C (1)	Cl (2)	Si (2)						
	14.7	9.9	10.4	11.7	14.9						
Zn:	Ba (3)	Mg (2)	P (4)	Y (3)							
	18.3	15.7	20.9	17.7							
Zr:	Al (5)	Au (1)	F (1)	Ga (1)	O (1)	Sb (2)	Se (1)	Si (1)			
	19.7	17.3	7.8	17.9	9.3	22.0	18.0	17.0			
Y:	Cd (1)	F (1)	Zn (1)								
	24.7	9.9	21.5								

Table 4. *Average relative deviation (%) from volume according to methods 1–4 (internal consistency)*

	Method 1	Method 2	Method 3	Method 4
Average relative deviation	39.5	20.5	16.0	6.5

methods 2 to 4, this being more pronounced between methods 3 and 4: on average, the volume variations within a family of A_mB_n compounds (A and B fixed; m and n variable) are of the order of 6%.

Thus there are indications that the use of Voronoi polyhedral volumes could be developed to provide a set of natural constants linking intrinsic atomic properties with their structures. However, although inner consistency may be observed within the data set used, whether or not the values found agree with results found for structures not used in the primary data set may be another matter entirely. In order to obtain an idea of this, which, in fact, is the ability to predict the volume requirements of different atom types in binary compounds given only information on the atom types present, Tables 2 and 3 have been used to predict the volumes for seven different arbitrarily chosen binary structures not contained in the primary data set. The results are presented in Table 5. They indicate that the 6% error level may not generally be reached in predictions; the average error, at 13.8%, for the 14 atom types in the test set, is more than twice as large. The average error for prediction of volume of a formula unit, and thereby prediction of density, is slightly smaller, at 12.6%; this is because the errors for the two atom types partly cancel each other out. Interestingly, the average error for the three intermetallic compounds, at 6%, is less than a third of the error for the four ionic compounds. Given the very small test set, of course, this must not be relied upon too heavily.

Three comparisons with related work should be mentioned. First, in work by Mackay (1972), where a Voronoi analysis was carried out for $Ba_3V_2O_8$, Ba polyhedral volumes were found to be *ca* 18 Å^3, the V volumes *ca* 8 Å^3 and the O polyhedral volumes approximately 17 Å^3. Whereas the agreement is fairly good for O (14.7 Å^3 would be predicted by Table 2, since both Ba and V are metals) and V (9.1 Å^3 would be predicted, since V is predominantly coordinated by O), the agreement for Ba is very poor: 32 Å^3 would be predicted from this work, suggesting that the polyhedral volume is very sensitive to the other atom type with

Table 5. *Predicted volumes (Å^3) for external data set*

FU: formula unit. V: volume (1–4 represent predicted values corresponding to methods 1–4; A is actual volume). dV: deviation from actual volume (value in % is relative to actual volume).

		UF_3			U_2F_9			FeS			Fe_3S_4			$MoNi_3$			$AuCu_3$			Au_3Cu		
		U	F	FU	U	F	FU	Fe	S	FU	Fe	S	FU	Mo	Ni	FU	Au	Cu	FU	Au	Cu	FU
V (Å^3)	1	18.1	18.1	72.4	18.1	18.1	199.1	18.1	18.1	36.2	18.1	18.1	126.7	18.1	18.1	72.4	18.1	18.1	72.4	18.1	18.1	72.4
	2	16.9	15.9	64.6	16.9	15.9	176.9	11.7	19.8	31.5	11.7	19.8	114.3	11.7	12.5	49.2	15.0	14.4	58.2	15.0	14.4	59.4
	3	13.3	15.1	58.6	13.3	15.1	162.5	11.5	19.1	30.6	11.5	19.1	110.9	12.5	12.5	50.0	15.0	14.1	57.3	15.0	14.1	59.1
	4	8.8	17.4	61.0	8.8	17.4	174.2	11.5	14.3	25.8	11.5	14.3	91.7	11.7	11.7	46.8	13.8	13.8	55.2	13.8	13.8	55.2
	A	12.1	13.3	52.1	9.3	14.8	152.0	14.3	15.9	30.2	15.3	18.7	120.6	11.9	11.9	47.6	13.2	13.2	52.7	15.6	15.6	62.4
dV (Å^3)	1	6.0	4.8	20.3	8.8	3.3	47.1	3.8	2.2	6.0	2.8	−0.6	6.1	6.2	6.2	24.8	4.9	4.9	19.7	2.5	2.5	10.0
	2	4.8	2.6	12.5	7.6	1.1	24.9	−2.6	3.9	1.3	−3.6	1.1	−6.3	−0.2	0.6	1.6	1.8	1.2	5.5	−0.6	−1.2	−3.0
	3	1.2	1.8	6.5	4.0	0.3	10.5	−2.8	3.2	0.4	−3.8	0.4	−9.7	0.6	0.6	2.4	1.8	0.9	4.6	−0.6	−1.5	−3.3
	4	−3.3	4.1	8.9	−0.5	2.6	22.2	−2.8	−1.6	−4.4	−3.8	−4.4	−28.9	−0.2	−0.2	−0.8	0.6	0.6	2.5	−1.8	−1.8	−7.2
dV (%)	1	49.7	35.6	38.9	95.2	22.0	31.0	26.3	14.2	19.9	18.3	−3.0	5.1	52.3	52.2	52.2	37.5	37.5	37.5	16.0	16.1	16.0
	2	39.8	19.1	23.9	82.2	7.2	16.4	−18.4	24.9	4.3	−23.6	6.1	−5.2	−1.6	5.1	3.4	14.0	9.4	10.5	−3.8	−7.6	−4.8
	3	10.0	13.1	12.4	43.4	1.8	6.9	−19.8	20.5	1.4	−24.9	2.4	−8.0	5.2	5.1	5.1	14.0	7.1	8.8	−3.8	−9.6	−5.3
	4	−27.2	30.4	17.0	−5.1	17.3	14.6	−19.8	−9.8	−14.5	−24.9	−23.4	−23.9	−1.6	−1.6	−1.6	4.9	4.8	4.8	−11.5	−11.5	−11.5

which Ba is combined. Furthermore, no explicit consideration of barium oxides has been made here.

Secondly, in work currently in progress by the authors on polynuclear aromatic hydrocarbons, the average volumes for C and H have been found to be 8.4 and 13.0 Å^3, respectively. The predictions from Table 2 are 10.4 Å^3 for C and 13.8 Å^3 for H. Although the agreement for C is only within 24%, the reasonably good agreement for H (around 6%) indicates that the gross structural requirements of H atoms are relatively invariant between organic and inorganic systems.

Thirdly, results by Koch & Fischer (1980), obtained using the radical-planes approach on a set of 192 organic crystals (giving volumes for C, O, N, H, F, Cl, Br and I) and tested against 167 other crystal structures, indicate predictability of volumes to within 15%. This is clearly better than the results obtained in the present study and suggests that predictability may be considerably improved by including larger numbers of structures in the analysis [the atom types studied by Koch & Fischer (1980) were only included in 74 of the compounds in the primary data set of the present work and, as these were binary, each individual atom type was included in far fewer compounds].

Having focused solely on Voronoi polyhedral volumes, the charge could be made that representative atomic volumes could alternatively be calculated by least-squares-fitting procedures applied to inter-related compounds and their structures. Against this, it should be pointed out that the Voronoi tessellation provides information directly on individual structures, *i.e.* it is a true analysis. Thus, the Voronoi approach generally leads to a higher level of detail, with the derivation of representative volumes (as with least-squares methods) an optional secondary procedure. The ability to analyse individual structures also opens up the possibility of studying interdependencies between different parameters (*e.g.* involving facial areas and vertices), as discussed in §1.1. Thus, the strength of the Voronoi tessellation is that it provides a set of unambiguous parameters ('tools') with which a structure may be quantified.

Comparison of the average errors for the four methods indicates the extent to which such tools are required to refine the approach: not even in the best case considered can Voronoi volumes be predicted with more than 6% accuracy, on average. The next step would be to include information on stoichiometry, undoubtedly allowing volumes to be predicted more accurately. This would require a much larger primary data set than that used here. After the inclusion of stoichiometry, no further global parameters are generally available, and the logical way to proceed would be to define a set of parameters by which the local atomic topology could be predicted, and then predict the volume of each atom given this surrounding environment. Again, this would probably lead to increased accuracy.

Ultimately, the extraction of truly atom-type typical values will require many parameters to be taken into consideration and a study of the interplay between them. Fortunately, there is nothing in principle to prevent this from being performed.

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