

Refitted tetrahedral covalent radii for solids

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The previous systems of molecular single-, double-, and triple-bond self-consistent, additive covalent radii $R(AB) = r(A) + r(B)$ are now completed with a fit for crystals, where both atoms are tetrahedrally coordinated. A self-consistent primary fit is carried out using elements such as Si and binary compounds such as GaAs or ZnS. Further checks involve also ternary compounds such as chalcopyrites, CuInS_2 , and the quaternary compounds $\text{Cu}_2\text{ZnSnS}_4$ and $\text{Cu}_2\text{ZnSnSe}_4$, the latter two with both kesterite and stannite structures. The input bond lengths R are taken from experimental or theoretical data. For the 30 elements in the primary fit, the mean-square deviation of the predicted $R(AB)$ values is only 0.67 pm for the 48 systems used. The results are compared to earlier radii by Pauling and Huggins [Z. Kristallogr. A **87**, 205 (1934)] or by Van Vechten and Phillips [Phys. Rev. B **2**, 2160 (1970)], and to the recent molecular covalent radii.

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I. INTRODUCTION

The aim of additive covalent radii is to express approximately a bond length as the sum of two atomic radii:

$$R_{AB} = r(A) + r(B). \quad (1)$$

We have recently presented sets of such covalent radii for single,¹ double,² and triple bonds³ primarily for molecules that are predominantly covalent. Another recent fit for single bonds, using the Cambridge Crystallographic Data Base, is that of Cordero *et al.*⁴ Our radii were fitted self-consistently to a data set, combining both experimental and calculated data points. Values were given up to the superheavy element $E118$; for a suggested periodic table up to $E172$, see Ref. 5. A mean-square deviation δ of about 3 pm was achieved for each of the three sets of radii. The later usage of these sets has given many further confirmations and no radical deviations.

We regard these radii, and Eq. (1), as purely operational. No attempt is made to relate them to basic theory. Concerning the bond orders, we defined for molecules a single bond as one, having a σ^2 electron pair in a bonding molecular orbital, as in ethane $\text{H}_3\text{C}-\text{CH}_3$, or having a corresponding net excess, as in Cl_2 . Similarly, double and triple bonds are defined as ones, having a $\sigma^2\pi^2$ or a $\sigma^2\pi^4$ bonding system, respectively. It then does not matter if alternative definitions, such as the effective bond order (EBO) of Roos *et al.*,⁶ would give lower bond orders than 2 or 3 for them, as long as the internal consistency of the distances is preserved. The criteria for multiple bonding were that the distances fit the system and that the two (σ and π) occupied orbitals can be found by visual inspection (for calculated data).

Two earlier sources for covalent radii are from Pauling^{7,8} and Batsanov.^{9,10} In purebred form, the radii are obtained by halving a homonuclear bond

$$r(E) = R(E - E)/2. \quad (2)$$

As said, our approach to covalent radii is that we treat all elements and all admitted data points as equal. All radii are then obtained self-consistently through a least-squares fit. Specific molecular coordination numbers (CN) and oxidation states were chosen in the previous, molecular, sets.

In the present case, we consider the effective covalent radii for crystals, where both atoms A and B are, exactly or

approximately, tetrahedrally coordinated. This set is expected to be of interest for both solid-state or materials scientists and chemists. As reviewed by Osten,¹¹ the question of interatomic distances in heteroepitaxial semiconductor structures is non-trivial and occasionally unsettled. Two prominent predecessors for tetrahedral radii are Pauling and Huggins¹² in 1934, or Van Vechten and Phillips¹³ in 1970. Both sets only used binary compounds. Pauling fixed the tetrahedral radius of sulfur as 106 pm, and many of the other radii were adjusted by *ad hoc* arguments.¹² Close to the present fit are the tetrahedral radii of Palatnik *et al.*¹⁴ They included in their fit ternary compounds and also had no electronegativity correction. A treatise on the tetrahedrally coordinated crystals was published by Parthé.¹⁵

The working equations are listed in Sec. VII. The homonuclear systems (2) also do introduce here a certain emphasis for the distances included in them [see Eq. (4)].

II. RESULTS AND DISCUSSION

In our single-bond fit,¹ we had to eliminate from the data set the TM- X bonds between transition metals and halogen atoms. These bonds actually have some π back donation from the $n\pi\pi(X)$ to the empty $(n' - 1)d\pi(M)$ orbitals of the metal. Therefore, they are partially multiple bonds, and too short. Then, the rest fitted well.

In order to check the consistency of main-group and transition-metal radii, we first performed a Fit 1 for the $N = 26$ data points and $N_{\text{at}} = 17$ elements, involving main-group elements only (see Table I). The resulting mean-square deviation δ was 0.54 pm. We then added the transition-metal compounds in Fit 2 ($N = 45$, $N_{\text{at}} = 30$, $\delta = 0.63$ pm). (The two data sets are coupled by nitrogen in ScN, and by O-Te.) Concerning the input data, useful general sources are Martin,¹⁶ Van Vechten and Phillips,¹³ and Vurgaftman *et al.*¹⁷ All these 45 points were experimental.

For the Group 11-17 bonds, there were available experimental data for only five binary compounds (CuF, CuCl, CuBr, CuI, and AgI) having tetrahedral local coordination, while there are six parameters $r(\text{Cu}, \text{Ag}; \text{F}, \text{Cl}, \text{Br}, \text{I})$. We therefore added the computed distances of Maeda *et al.*¹⁸ for CuESe_2 , CuESe_2 , and AgESe_2 , average for $E = \text{Al}, \text{In}, \text{Ga}$ taken. Their calculated distances are close to experiment. This final fit had $N = 48$,

TABLE I. The input data used in the fit. R (in pm) is the interatomic distance. The points up to InSb were used in Fit 1. The points ScN to HgTe were added in Fit 2. ZB represents zinc-blende and W represents wurtzite.

Z_1	Z_2	R	Species	Ref.
6	6	154.5	C (diamond)	16
6	6	154.5	C (lonsdaleite)	24
14	14	235.2	Si	16
32	32	244.96	Ge	16
50	50	280.0	Sn(gray)	31
4	16	210.9	BeS (ZB)	32
4	34	219.5	BeSe	13
4	52	239.9	BeTe	13
5	7	156.5	BN (ZB)	13
5	7	156.5	BN (W)	24
5	15	196.5	BP	13
5	33	206.85	BAs	33
7	31	196.2	GaN	34
7	49	215.6	InN	34
12	16	245.1	MgS	35 and 36
12	34	255.0	MgSe	35
12	52	275.4	MgTe	37
13	15	236.7	AlP	17
13	33	245.1	AlAs	17
13	51	265.7	AlSb	17
15	31	236.0	GaP	17
15	49	253.42	InP	38
31	33	244.8	GaAs	17
31	51	263.96	GaSb	17
33	49	262.3	InAs	17
49	51	280.6	InSb	17
7	21	207.49	ScN (W)	39
8	27	193.0	CoO	40
8	30	197.8	ZnO (W)	41
9	29	184.6	CuF	42
16	25	243.1	β -MnS	43
16	29	230.0	CuES ₂ ^a	18
16	30	234.2	ZnS	13
16	48	251.9	CdS (ZB)	34
16	80	253.38	HgS (ZB)	44
17	29	234.70	CuCl	45
25	34	255.35	MnSe (W)	46
29	34	242.8	CuESe ₂ ^a	18
29	35	246.62	CuBr	45
29	53	262.17	CuI	45
30	34	245.4	ZnSe	16
30	52	263.7	ZnTe	13
34	47	262.9	AgESe ₂ ^a	18
34	48	263.3	CdSe (ZB)	13
47	53	281.0	AgI (ZB)	47
48	52	280.6	CdTe	48
52	80	279.6	HgTe	48

^aAverage for $E = \text{Al, Ga, In}$.

$N_{\text{at}} = 30$, $\delta = 0.67$ pm. It yielded the Group 11 and 17 radii in the Fit 2 of Table IV. The quality of Fit 2 for the 45 fitted points is shown in Fig. 1. Some outlier points were eliminated from the data before the mentioned fits. They are shown in Table II, and discussed below.

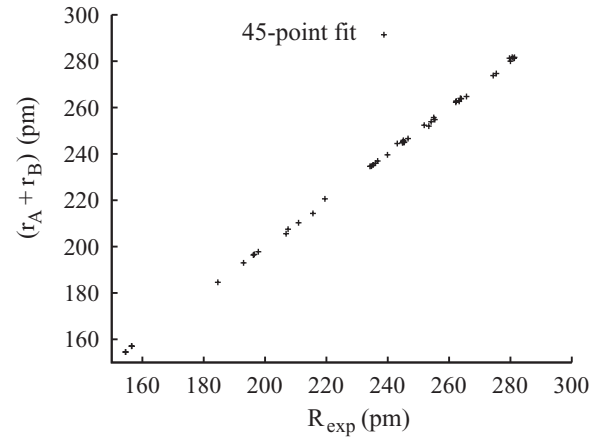


FIG. 1. A comparison of the predicted bond lengths $r_{\text{T}}(\text{A}) + r_{\text{T}}(\text{B})$ with the experimental $R(\text{AB})$ values for the 45-point data set in Table I for periods 2 to 6.

Finally, a few elements (Li, Fe, Tl, Pb, Bi, Po), the data in Table III of which would have otherwise increased δ , were treated perturbatively by keeping the 30 self-consistent radii of Fit 2 fixed. For general purpose use, we recommend Fit 2. The same results are shown in Fig. 2.

III. COMPARISON WITH PREVIOUS SETS

A comparison with the earlier r_{T} of Pauling,⁸ van Vechten and Phillips,¹³ and Palatnik¹⁴ is shown in Table IV and Fig. 3. The molecular single-bond radii r_1 of Pyykkö and Atsumi¹ and Cordero *et al.*⁴ are also shown. We first notice that our radii are both spiritually and numerically close to those of Pauling, when the latter are available. In particular, the Be and Mg values are close. Some deviations occur for the halogens. For Cl-I, our tetrahedral halogens are larger than those of Pauling. Concomitantly, our Cu and Ag are smaller. Note that these smaller $r_{\text{T}}(\text{Cu, Ag})$ fit the $M-E$ ($E = \text{S, Se}$) distances in ternary and quaternary compounds (see Table V). Therefore, they may be a better choice for general tetrahedral radii.

Concerning Van Vechten and Phillips,¹³ many of their values (the nonunderlined ones in their Table I) seem to be simply assumed and fixed for an entire row of elements. This is bound to affect also their partners, notably Be and Mg. For practical estimates of bond lengths, it may be desirable to replace their entire system by the present one. When available, the Palatnik radii¹⁴ are close to the present ones, some deviations occurring in Group 11 (Cu, Ag), Group 12 (Zn-Hg), and in the fourth period for Te and I.

TABLE II. List of some outlier data points, which are not included in the fit. The radii r refer to Fit 2 in Table IV.

Z_1	Z_2	Species	$r_{\text{A}} + r_{\text{B}}$	$R(\text{AB})$	Ref.
4	8	BeO (W)	173.5	164.9 ^a	49
6	14	SiC	194.9	188.27 ^a	13
7	13	AlN	197.4	189.2 ^a	13
80	84	HgPo (ZB)	289.4	298.0 ^b	50

^a R too short, compared to present radii.

^b R too long, compared to present radii.

TABLE III. Data, used for perturbative fits of $r(E)$ to other Fit 2 radii.

E	Z_1	Z_2	R (pm)	Species	Ref.
Li	3	35	252.5	β -LiBr	51
	3	53	275.7	β -LiI	52
Fe	16	26	225.7	CuFeS ₂	53
	16	26	224.6	AgFeS ₂	54
Tl	34	81	220–225	CuTlSe ₂	55
Pb	6	82	222.5	PbC	56
	14	82	261.8	PbSi	56
	32	82	266.5	PbGe	56
	50	82	283.1	PbSn	56
Bi	5	83	233.4	BBi	57
	13	83	274.6	AlBi	57
	31	83	274.1	GaBi	57
Po	30	84	273.19	ZnPo	50
	48	84	288.60	CdPo	50

Concerning the various groups of the periodic table, we note the following:

(i) *Group 1*. We now have produced an $r_T(\text{Li})$ using recent data for β -LiBr and β -LiI. It is further supported by the data for LiPN₂ and LiInTe₂ in Table V.

(ii) *Group 3*. Here the only entry is Sc.

(iii) *Groups 7–9*. These 3d metals have a divalent state. Tetrahedral radii are given for Mn, Fe, and Co. For the 3d transition metals, Iwanowski *et al.*¹⁹ quote radii of 130.2, 123.9, 119.7, and 113.0 pm for Mn, Fe, Co, and Ni, respectively, assuming the $r_T(\text{Zn})$ of 122.5 pm.¹³

(iv) *Group 11*. Radii for Cu and Ag are given. For Au, the tetrahedral coordination is rare.

(v) *Group 12*. Radii for Zn, Cd, and Hg are given. For Hg, the HgSe point in Table V supports the HgS and HgTe ones.

(vi) *Group 13*. Radii for B-Tl are given. Note that Ga is slightly smaller than Al, an effect attributed to partial screening by the 3d shell for Ga.²⁰

(vii) *Group 14*. Radii for C-Pb are given.

(viii) *Group 15*. Radii for N-Bi are given.

(ix) *Group 16*. Radii for O-Po are given.

(x) *Group 17*. Radii for F-I are given. For the peculiarities of the fluorine atom, see Ref. 1. Note that these tetrahedral radii for coordination number $CN = 4$ are larger than the molecular r_1 in Table IV. These molecules mostly had $CN = 1$ for halogens.

(xi) *Periodic trends*. In period 4 (K-Kr), Sc [taken as Sc(III), $3d^0$] is smaller than Mn, taken as Mn(II), $3d^5$. Otherwise, along a period, the r_T systematically decrease.

As function of the row, the main-group elements show the trend $2p \ll 3p < 4p < 5p \leq 6p$. Note here the anomalously small size of the nodeless $2p$ shell.^{20,21}

IV. THE OUTLIERS

Perhaps the most interesting outlier is SiC. As already noted by Pauling²² or Van Vechten and Phillips,¹³ the bonds of silicon carbide are shorter than those predicted by the covalent radii of Si and C. Pauling attributed the shortening to additional, ionic contributions. Pitzer²³ evoked differences in core repulsion between 2nd-period ($2s2p$) and 3rd-period ($3s3p$) elements to explain it. Van Vechten and Phillips¹³ also invoke core effects. A further reason could be the involvement of Si 3d orbitals, leading to partial multiple bonding. As far as the shorter bonds reflect stronger bonding, it would be interesting to understand why carborundum is so hard. Moreover, it then is only natural that some other isoelectronic systems (AlN) become outliers (see Table II).

V. FURTHER VALIDATION

We note first that most of our input data was for elements of Group 14, and for the binary combinations of Groups 13-15

Tetrahedral Covalent Radii (pm)

Atomic number Symbol Radius in pm																					
1 H																	2 He				
3 Li 137	4 Be 106.1															5 B 88.2	6 C 77.3	7 N 68.9	8 O 67.4	9 F 57.5	10 Ne
11 Na	12 Mg 141.2															13 Al 128.5	14 Si 117.6	15 P 108.4	16 S 104.2	17 Cl 107.6	18 Ar
19 K	20 Ca	21 Sc 138.6	22 Ti	23 V	24 Cr	25 Mn 140.3	26 Fe 120.9	27 Co 125.6	28 Ni	29 Cu 127.1	30 Zn 130.4	31 Ga 127.5	32 Ge 122.5	33 As 117.4	34 Se 114.5	35 Br 119.5	36 Kr				
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag 147.3	48 Cd 148.2	49 In 145.5	50 Sn 140.0	51 Sb 136.3	52 Te 133.5	53 I 134.5	54 Xe				
55 Cs	56 Ba	La-Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg 147.8	81 Tl 138	82 Pb 144.1	83 Bi 146.0	84 Po 141.6	85 At	86 Rn				

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FIG. 2. The present radii from Fit 2.

TABLE IV. Comparisons of present tetrahedral covalent radii r_T from Fits 1 and 2 (see text) with the earlier values of Pauling (Ref. 8), van Vechten and Phillips (Ref. 13), and Palatnik (Ref. 14). The molecular single-bond radii r_1 are shown for comparison.

Z	E	r_T					r_1	
		Fit 1	Fit 2	Ref. 8	Ref. 13	Ref. 14	Ref. 1	Ref. 4
3	Li		137 ^a				133	128
4	Be	106.1	106.1	106	97.5		102	96
5	B	88.6	88.2	88	85.3		85	84
6	C	77.3	77.3	77	77.4		75	76
7	N	68.5	68.9	70	71.9	70	71	71
8	O		67.4	66	67.8		63	66
9	F		57.5	64	67.2 ^b		64	57
12	Mg	141.1	141.2	140	130.1	140	139	141
13	Al	128.8	128.5	126	123.0	131.7	126	121
14	Si	117.6	117.6	117	117.3	117	116	111
15	P	108.1	108.4	110	112.8	110	111	107
16	S	104.4	104.2	104	112.7 ^b	104	103	105
17	Cl		107.6	99	112.7 ^b		99	102
21	Sc		138.6				148	170
25	Mn		140.3				119	150
26	Fe		120.9 ^a				116	142
27	Co		125.6				111	138
29	Cu		127.1	135	122.5 ^b	136	112	132
30	Zn		130.4	131	122.5 ^b	139	118	122
31	Ga	127.8	127.5	126	122.5 ^b	131.5	124	122
32	Ge	122.5	122.5	122.5	122.5 ^b		121	120
33	As	117.1	117.4	118	122.5 ^b	117	121	119
34	Se	113.6	114.5	114	122.5 ^b	114.5	116	120
35	Br		119.5	111	122.5 ^b	120	114	120
47	Ag		147.3	152	140.5 ^b	155	128	145
48	Cd		148.2	148	140.5 ^b	156.5	136	144
49	In	145.8	145.5	144	140.5 ^b	148.5	142	142
50	Sn	140.0	140.0	140.5	140.5		140	139
51	Sb	136.0	136.3	136	140.5 ^b	135	140	139
52	Te	134.0	133.5	132	140.5 ^b	128	136	138
53	I		134.5	128	140.5 ^b	113.4	133	139
80	Hg		147.8			154.5	133	132
81	Tl		138. ^a			154.2	144	145
82	Pb		144.1 ^a				144	146
83	Bi		146.0 ^a				151	148
84	Po		141.6 ^a				145	140

^aPerturbative value, fitted to other Fit 2 radii using data in Table III.

^bNot underlined in their Table I.

(III-V), 12-16, 2-16, and 11-17. In the case of hexagonal C and BN, the data of Yoshiasa *et al.*²⁴ in Table V show differences between the one apical and three basal distances, but the average is the same as for the cubic structure. Concerning other combinations, the first such system is the supertetrahedral T4-ZnGaSnSeS cluster of Wu *et al.*²⁵ Its Zn-S and Zn-Se distances are close to the bulk ones in Table I. The four others in Table V are in a reasonable agreement with the radii.

Another rather complicated structure is Ag₂HgSnSe₄ where all atoms are said to have $CN = 4$.²⁶ The three average distances for cases with four equal ligands in Table V are coherent with the present radii. There is one short Sn-Se distance of 232 pm, which is even inside the sum of the triple-bond radii³ r_3 , or 239 pm. In the case of the quaternary small-gap semiconductors of type Cu₂MSnE₄; $M = \text{Fe, Zn, Cd, Hg}$; $E = \text{S, Se}$ (I₂-II-IV-VI₄), there are both x-ray structures^{27,28}

and recent density functional theory (DFT) calculations.^{29,30} Two distinct tetragonal structures, kesterite and stannite, may occur. All local atomic coordinations are closely tetrahedral. For a comparison with present radii, see Table V.

Finally, we give in Table VI a separate comparison of the present predictions against calculated distances for the intra-Group 14 binary combinations, calibrated against SiC. For the other five combinations (excluding Pb), theoretical data are available

VI. CONCLUSIONS

The remarkable thing is that the present, simple fit of an additive covalent radius $r(E)$ to each element E is able to predict the bond lengths R below 1 pm statistical error inside the present data sets. Outside them, these radii

TABLE V. Some further tests on the present radii. KS = kesterite, ST = stannite, W = wurzite, ZB = zinc-blende.

Z_1	Z_2	Species	$r_A + r_B$	$R(AB)$	Ref.
6	6	C(lonsdaleite)(av)	154.6	154.5	24
		C(lonsdaleite)(apical)		159(4)	24
		C(lonsdaleite)(basal)		153(2)	24
5	7	BN(W)(av)	157.2	156.5	24
		BN(W) (apical)		164(3)	24
		BN(W) (basal)		154(1)	24
3	7	LiPN ₂	206.	210.0	58
3	52	LiInTe ₂	270.5	272.5	59
49	52	LiInTe ₂	279.0	276.8	59
16	31	T4-ZnGaSnSeS cluster	232	223–232	25
16	50	T4-ZnGaSnSeS cluster	244	239–245	25
31	34	T4-ZnGaSnSeS cluster	242	237–242	25
34	50	T4-ZnGaSnSeS cluster	254	242–256	25
16	29	Cu ₂ ZnSnS ₄	231.3	233.0, 233.2 (KS)	27
		Cu ₂ ZnSnS ₄		232.0 (ST)	27
		Cu ₂ ZnSnS ₄		226.5 (KS) ^a	30
		Cu ₂ ZnSnS ₄		229.5 (KS) ^a	29
16	30	Cu ₂ ZnSnS ₄	234.6	233.6 (KS)	27
		Cu ₂ ZnSnS ₄		234.8 (ST)	27
		Cu ₂ ZnSnS ₄		231.3 (KS) ^a	30
		Cu ₂ ZnSnS ₄		234.9 (KS) ^a	29
16	50	Cu ₂ ZnSnS ₄	244.2	241.1 (ST)	27
		Cu ₂ ZnSnS ₄		238.5 (ST) ^a	30
		Cu ₂ ZnSnS ₄		247.5 (ST) ^a	29
29	34	Cu ₂ ZnSnSe ₄	241.6	243.6 (ST)	28
		Cu ₂ ZnSnSe ₄		236.7 (ST) ^a	30
		Cu ₂ ZnSnSe ₄		239.0 (ST) ^a	29
30	34	Cu ₂ ZnSnSe ₄	244.9	242.6 (ST)	28
		Cu ₂ ZnSnSe ₄		244.5 (ST) ^a	30
		Cu ₂ ZnSnSe ₄		246.6 (ST) ^a	29
34	50	Cu ₂ ZnSnSe ₄	254.5	253.9 (ST)	28
		Cu ₂ ZnSnSe ₄		253.4 (ST) ^a	30
		Cu ₂ ZnSnSe ₄		260.7 (ST) ^a	29
34	48	Cu ₂ CdSnSe ₄	262.7	267.0 (ST)	28
34	50	Cu ₂ CdSnSe ₄	254.5	251.3 (ST)	28
34	80	Cu ₂ HgSnSe ₄	262.3	265.7 (ST)	28
34	50	Cu ₂ HgSnSe ₄	254.5	253.9 (ST)	28
32	34	Cu ₂ ZnGeSe ₄	237	237.1 (ST)	60
34	47	Ag ₂ HgSnSe ₄	261.8	266.7 ^b	26
34	50	Ag ₂ HgSnSe ₄	254.5	250.6 (av)	26
34	80	Ag ₂ HgSnSe ₄	262.3	257.3 (av)	26
16	29	CuFeS ₂	231.3	230.2	53
16	26	CuFeS ₂	225.1	225.7	53
16	47	AgFeS ₂	251.5	246.98	54
16	26	AgFeS ₂	225.1	224.58	54
7	14	MgSiN ₂	186.5	176	67
7	25	MnSiN ₂	209.2	211.5	61
7	32	MnGeN ₂	191.4	197.1	62
15	25	MnGeP ₂	248.7	240.8	63
34	80	HgSe(ZB)	262.3	263.5	64

^aDFT.^bAv. of 259, 261.6, 268.1, and 278.

allow fast estimates in unknown cases, such as various ternary and quaternary minerals or semiconductor structures. Our radii mainly deviate from Pauling's tetrahedral radii in having smaller coinage metals (Cu, Ag) and larger

halogens (Cl, Br, I). The experimental data for chalcopyrites (such as CuFeS₂) or kesterites and stannites (such as Cu₂ZnSnS₄) support this choice, giving it some objective validity.

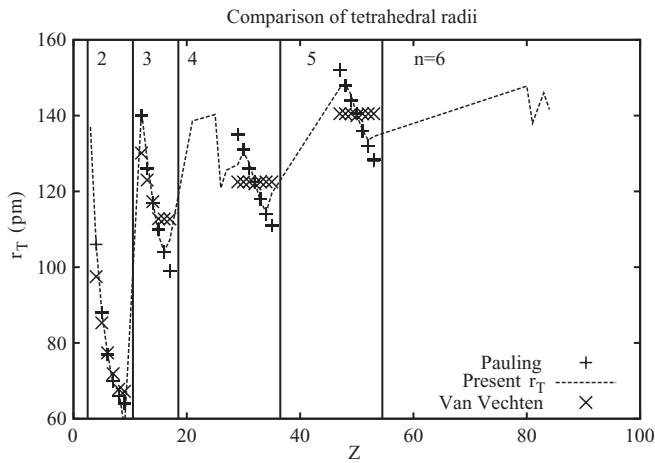


FIG. 3. A comparison of the present radii, given by the line, with those of Pauling (Ref. 8) or Van Vechten and Phillips (Ref. 13).

VII. COMPUTATIONAL DETAILS

The same iterative program was used as in the earlier single-, double-, and triple-bond work.^{1–3} It is based on the penalty function over homonuclear and heteronuclear pairs

$$\sum_k (\Delta_k)^2 = \sum_i^{K_{\text{homo}}} (R_{ii} - 2r_i)^2 + \sum_{ij}^{K_{\text{hetero}}} (R_{ij} - r_i - r_j)^2. \quad (3)$$

TABLE VI. Tests of the present radii on binary Group-14 compounds with an assumed zinc-blende structure. All values in pm.

Z ₁	Z ₂	Comp.	r _A + r _B	R(AB)			
				Expt.	Ref. 65	Ref. 66	Ref. 56
6	14	SiC	194.9	188.27	187.2	187.0	186.8
6	32	GeC	199.8		195.7		194.8
6	50	SnC	217.3		209.4		214.8
14	32	GeSi	240.1		239.0	236.9	236.9
14	50	SnSi	257.6		257.8		256.1
32	50	SnGe	262.5		262.1		260.0

Setting its derivatives with respect to r_i equal to zero, one obtains the iterative algorithm

$$r_i^{(N+1)} = \frac{1}{4K_{\text{homo}} + K_{\text{hetero}}} \left[\sum_i^{K_{\text{homo}}} 2R_{ii} + \sum_j^{K_{\text{hetero}}} (R_{ij} - r_j^{(N)}) \right]. \quad (4)$$

Here, K is the number of data points in each set and N the iteration. No convergence difficulties or signs for multiple minima were noticed. The final data set (Table I) had 48 points, used for fitting the 30 r_T values given. The standard deviation

$$\delta = \left[\left(\sum_{\text{tot}}^K \Delta^2 \right) / K_{\text{tot}} \right]^{\frac{1}{2}}, \quad K_{\text{tot}} = K_{\text{homo}} + K_{\text{hetero}} \quad (5)$$

was then 0.67 pm. As said, six further elements were added perturbatively.

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