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Correlation between pseudopotential radii and interatomic distance and evaluation of bond characters for transition and lanthanide elements

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Abstract

On the basis of a simple sp-bonding scheme, an empirical linear correlation is obtained between interatomic distances of elemental substances and the weighted average pseudopotential radii which are calculated from Zunger's s and p pseudopotential radii by considering the outermost electronic configuration. Using this empirical linear correlation and the weighted pseudopotential radii, interatomic distances of 178 closed- and open-shell sp-bonded compounds are calculated within 10% accuracy with the exception of only a few compounds. It is suggested that deviations of the calculated interatomic distances from the observed values arise from the differences in d electron contributions, high covalencies and some contributions of p-character in the light $(ns)^N$ elements. Again with the exception of only a few compounds, interatomic distances for 101 transition metal and 242 lanthanide compounds are also reproduced within 10% accuracy by the effective pseudopotential radii of these elements, which are determined by the empirical correlation for sp-bonded elemental substances and the pseudopotential radii of Zunger. Furthermore, the ratios of the sd hybridization effect in transition elements and lanthanide elements are proposed on the basis of this empirical correlation.

Keywords: Pseudopotential radius; Interatomic distances; Bond character; sd hybridization; Lanthanides

1. Introduction

The importance of interatomic distance in crystalline materials has been underlined by many investigators, especially in the context of atomic and ionic radii [1–5]. Furthermore, a close connection of interatomic distances with the bond character in the crystalline state was proposed [6]. According to Van Vechten and Phillips [7,8], the interatomic distance is correlated with the covalency (or ionicity) of A^NB^{8-N} octet compounds, and band gaps of the compounds can be estimated using the formula $E_h = 40d^{-2.5}$, where d is the interatomic distance for the A–B bond in these AB compounds. Harrison pointed out that matrix elements in the energy matrix for band gap calculation can be formulated using the interatomic distance [9,10]. Thus the interatomic distance is the essential parameter for estimating the bond character of solid state materials.

In previous studies [11–13], it has been indicated that orbital electronegativities, which are derived from Zunger's pseudopotential radii [14], are effective for estimating the band gaps of various binary compounds, and for constructing the two band parameters (hybrid function H and gap reduction parameter S), which are successfully used in classifying various crystal structures. In these studies, however, the bond mode for calculation of the two band parameters, taking into account the bond character, has been assumed roughly for respective A–B bonding, especially for transition elements (for example, 50% sd contribution in late 3d transition metal elements). Although structural maps can be constructed using these parameters as structural coordinates, the respective bond mode or ratio of d electron contribution needs to be determined more precisely in order to obtain more precise numerical values of the two band parameters for each bonding.

For lanthanides, it is generally supposed that 4f electrons do not contribute significantly to their characteristic properties because they are more tightly bound to the nucleus. However, delicate contributions of 4f electrons to chemical bonds cause anomalies in systematic trends of various properties of lanthanides [15], e.g. the valence state of Ce^{4+}, Eu^{2+} and Yb^{2+} and very low melting points of light lanthanides. Although it has been supposed that these anomalies arise from 4f hybridization with 5d and 6s valence electrons [16], until now no clear understanding of these hybridizations has been firmly established. Thus, the contribution of d electrons through f–d hybridization and/or interaction between f levels and sd bands is important for understanding various anomalies of lanthanide compounds [17].

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In order to determine the d electron contribution, in the present study, the correlation between the interatomic distance and Zunger's pseudopotential radius is examined in elemental substances as a first step. Secondly, we examined whether the interatomic distances for various sp-bonded compounds can be calculated using the empirical relation for elemental substances. Lastly, we tried to estimate the d electron contributions of transition and lanthanide elements through the empirical relation between interatomic distances and Zunger's pseudopotential radii for elemental substances.

2. Pseudopotential radii and interatomic distances in elemental sp-bonded substances

First of all, we examine the correlation between average pseudopotential radii in sp-bonded elemental substances not including transition and post-transition elements as well as lanthanide elements. As described in Section 1, we use Zunger's pseudopotential radii in the present study. When an sp bond is formed by s and p electrons, the bond length, that is the interatomic distance, will be correlated with some average of the pseudopotential radii of these electrons, although the value of the average may depend on the mixing ratio between these electrons. In this study, the values of s and p pseudopotential radii are weighted by considering the outermost electronic configuration in the atomic state. For the elemental substances belonging to Groups Ia and IIa, the pseudopotential radius of the s electron is used by assuming no contribution of p electrons. The weighted average pseudopotential radii for sp-bonded elements are given in Table 1.

Table 1
Weighted average pseudopotential radii r_{ps} of sp-bonded elements based on the configuration of valence electrons and the observed interatomic distances d(obs)

Element	r_{ps}	EC	r_Σ	d(obs)
H	0.12_6	s	0.25_2	0.746
Li	0.985	s	1.97	3.039
Be	0.64	s^2	1.28	2.226
B	0.42_5	s^2p	0.85	1.589
C	0.32	s^2p^2	0.64	1.545
N	0.25_8	s^2p^3	0.51_6	1.098
O	0.21_5	s^2p^4	0.43	1.208
F	0.18_2	s^2p^5	0.36_4	1.417
Na	1.10	s	2.20	3.716
Mg	0.90	s^2	1.80	3.197
Al	0.81_5	s^2p	1.63	2.863
Si	0.71	s^2p^2	1.42	2.352
P	0.62_4	s^2p^3	1.24_8	2.21
S	0.55_3	s^2p^4	1.10_6	2.07
Cl	0.50_7	s^2p^5	1.01_4	1.988
K	1.54	s	3.08	4.544
Ca	1.32	s^2	2.64	3.947
Ga	0.81_8	s^2p	1.63_6	2.442
Ge	0.78	s^2p^2	1.56	2.450
As	0.71_5	s^2p^3	1.43	2.49
Se	0.65_2	s^2p^4	1.30_4	2.321
Br	0.60_9	s^2p^5	1.21_8	2.290
Rb	1.67	s	3.34	4.95
Sr	1.42	s^2	2.84	4.302
In	0.99_7	s^2p	1.99_4	3.251
Sn	0.94	s^2p^2	1.88	2.810
Sb	0.89_3	s^2p^3	1.78_6	2.90
Te	0.85	s^2p^4	1.70	2.846
I	0.80_9	s^2p^5	1.61_8	2.662
Cs	1.71	s	3.42	5.309
Ba	1.515	s^2	3.03	4.347
Tl	1.08_3	s^2p	2.16_6	3.408
Pb	1.04_5	s^2p^2	2.09	3.500
Bi	1.01_4	s^2p^3	2.02_8	3.09
Po	0.97_3	s^2p^4	1.94_6	3.345
At	0.94_3	s^2p^5	1.88_6	

r_Σ sum of weighted average pseudopotential radii, EC electronic configuration.

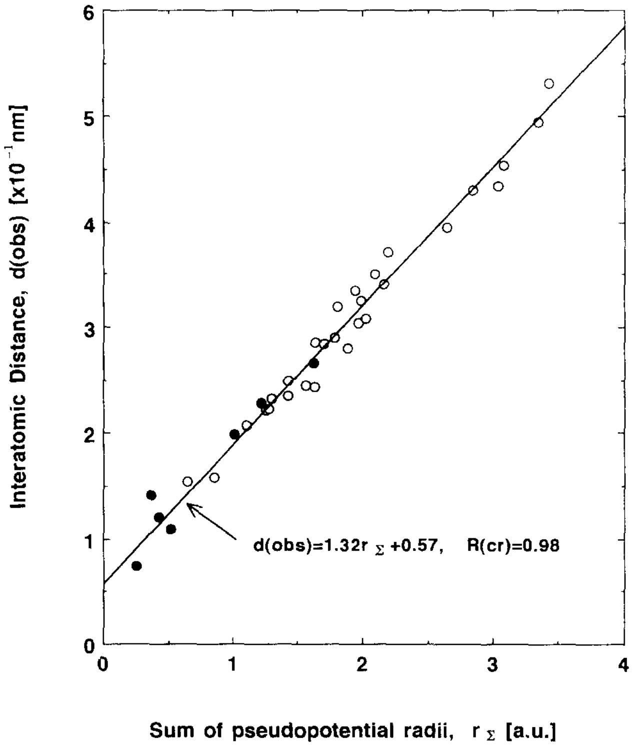

Fig. 1. Correlation between the sum of weighted average pseudopotential radii and the observed interatomic distance for 28 sp-bonded elemental substances. Solid circles show elemental substances with molecular state and these are excluded from calculation of the linear correlation.

The correlation between the sum of the weighted average pseudopotential radius and the observed interatomic distance for 28 sp-bonded elemental substances is shown in Fig. 1; molecular substances were not included for calculation of the linear correlation. All the data on interatomic distance are quoted from Ref. [18]. Quite good linearity is obtained and the correlation coefficient of the straight line is 0.98. This empirical correlation with quite high linearity suggests that the interatomic distances of crystalline substances can be predicted from these pseudopotential radii as long as the simple assumption on sp bonding is permitted. Data for molecular substances do not deviate far from the straight line in Fig. 1 but the linearity becomes worse.

3. Pseudopotential radii and interatomic distance in sp-bonded compounds

3.1. Closed-shell sp-bonded compounds

The existence of a correlation between the interatomic distance and sum of the weighted average pseudopotential radii for sp-bonded elemental substances can be confirmed if the interatomic distances of various sp-bonded compounds can be determined using the empirical correlation. Firstly, the reproducibility of the linear correlation between interatomic distance and sum of weighted average pseudopotential radii is examined for closed-shell sp-bonded compounds. Table 2 shows, for 118 sp-bonded compounds used in this study, the interatomic distances observed [8,19,20] and the sums of the weighted average pseudopotential radii for these sp-bonded compounds. (Except for interatomic distances quoted from Refs. [8] and [19], all interatomic distances of compounds are from Ref. [20]. The newest numerical value is selected when more than one interatomic distance has been reported for the same compound.) As is shown in Fig. 2, except for $SiTe_2$, all closed-shell sp-bonded compounds are placed very close to the straight line obtained empirically for sp-bonded elemental substances. All the data, except for $SiTe_2$, are plotted within 10% accuracy for the interatomic distances calculated from the empirical equation in Fig. 1. The values of deviation are calculated using the equation $[d(\mathrm{cal}) - d(\mathrm{obs})]/d(\mathrm{cal})$, where $d(\mathrm{cal})$ and $d(\mathrm{obs})$ are the

Table 2
Data of interatomic distances $d(\mathrm{obs})$ and sums r_Σ of the weighted pseudopotential radii for closed-shell sp-bonded compounds

	d(obs)	r_Σ	Reference		d(obs)	r_Σ	Reference		d(obs)	r_Σ	Reference
LiF	2.009	1.16_7	19	BeO	1.649	0.85_5	8	BeF_2	1.543	0.82_2	20
NaF	2.310	1.28_2	19	MgO	2.106	1.11_5	19	MgF_2	1.989	1.08_2	20
KF	2.674	1.72_2	19	CaO	2.405	1.53_5	19	CaF_2	2.366	1.50_2	19
RbF	2.820	1.85_2	19	SrO	2.580	1.63_5	19	SrF_2	2.511	1.60_2	19
CsF	3.004	1.89_2	19	BaO	2.762	1.73_0	19	BaF_2	3.021	1.69_7	19
LiCl	2.565	1.49_2	19	BeS	2.105	1.19_3	19	$BeCl_2$	2.02	1.14_7	20
NaCl	2.820	1.60_7	19	MgS	2.410	1.45_3	8	$MgCl_2$	2.51	1.40_7	20
KCl	3.146	2.04_7	19	CaS	2.845	1.87_3	19	$CaCl_2$	2.74	1.82_7	20
RbCl	3.291	2.17_7	19	SrS	3.010	1.97_3	19	$SrCl_2$	3.021	1.92_7	19
CsCl	3.571	2.21_7	19	BaS	3.194	2.06_6	19	$BaCl_2$	3.20	2.02_2	20
LiBr	2.751	1.59_4	19	BeSe	2.225	1.29_2	19	$BeBr_2$	–	–	–
NaBr	2.987	1.70_9	19	MgSe	2.762	1.55_2	19	$MgBr_2$	–	–	–
KBr	3.299	2.14_9	19	CaSe	2.955	1.97_2	19	$CaBr_2$	2.89	1.92_9	20
RbBr	3.427	2.27_9	19	SrSe	3.115	2.07_2	19	$SrBr_2$	3.20	2.02_9	20
CsBr	3.712	2.31_9	19	BaSe	3.330	2.16_7	19	$BaBr_2$	3.35	2.12_4	20
LiI	3.000	1.79_4	19	BeTe	2.436	1.49_0	19	BeI_2	–	–	–
NaI	3.236	1.90_9	19	MgTe	2.762	1.75_0	8	MgI_2	–	–	–
KI	3.533	2.34_9	19	CaTe	3.173	2.17_0	19	CaI_2	–	–	–
RbI	3.671	2.47_9	19	SrTe	3.235	2.27_0	19	SrI_2	3.338	2.22_9	20
CsI	3.955	2.51_9	19	BaTe	3.493	2.36_5	19	BaI_2	3.63	2.32_4	20
BN	1.565	0.68_3	8	Li_2O	2.004	1.20_0	19	Al_2O_3	1.92	1.03_0	20
BP	1.965	1.04_9	8	Na_2O	2.41	1.31_5	19	Al_2Se_3	2.37	1.46_7	20
BAs	2.069	1.14_0	8	K_2O	2.792	1.75_5	19	Ga_2O_3	1.83	1.03_3	20
AlN	1.892	1.07_3	8	Rb_2O	2.919	1.88_5	19	Ga_2S_3	2.243	1.37_1	19
AlP	2.360	1.43_9	8	Li_2S	2.472	1.53_8	19	Ga_2Se_3	2.351	1.47_0	19
AlAs	2.451	1.53_0	8	Na_2S	2.826	1.65_3	19	Ga_2Te_3	2.555	1.66_8	19
AlSb	2.656	1.70_8	8	K_2S	3.200	2.09_3	19	In_2O_3	2.27	1.21_2	20
GaN	1.944	1.07_6	8	Rb_2S	3.31	2.22_3	19	In_2S_3	2.58	1.55_0	20
GaP	2.360	1.44_2	8	Li_2Se	2.605	1.63_7	19	In_2Se_3	2.68	1.64_9	20
GaAs	2.441	1.55_3	8	Na_2Se	2.948	1.75_2	19	In_2Te_3	2.822	1.84_7	19
GaSb	2.649	1.71_1	8	K_2Se	3.324	2.19_2	19	Tl_2O_3	2.26	1.29_8	20
InN	2.154	1.25_5	8	Li_2Te	2.822	1.83_5	19				
InP	2.541	1.62_1	8	Na_2Te	3.167	1.95_0	19	SiO_2	1.87	0.92_5	20
InAs	2.614	1.71_2	8	K_2Te	3.530	2.39_0	19	SiS_2	2.133	1.26_3	20
InSb	2.806	1.89_0	8	Be_3N_2	1.89	0.89_8	20	$SiSe_2$	2.275	1.36_2	20
InBi	3.49	2.01_1	20	Mg_3N_2	2.14	1.15_8	20	$SiTe_2$	3.04	1.56_0	20
SiC	1.883	1.03_0	8	Ca_3N_2	2.46	1.57_8	20	GeO_2	1.89	0.99_5	20
								GeS_2	2.21	1.33_3	20
AlF_3	1.794	0.99_7	20	Be_3P_2	2.20	1.26_4	20	$GeSe_2$	2.354	1.43_2	20
GaF_3	1.89	1.00_0	20	Ba_3P_2	3.40	2.13_9	20	SnO_2	2.054	1.15_5	20
InF_3	2.053	1.17_9	20	Li_3N	2.05	1.24_3	20	SnS_2	2.56	1.49_3	20
TlF_3	2.29	1.26_5	20	Mg_3Sb_2	2.98	1.79_3	20	PbO_2	2.163	1.26_0	20

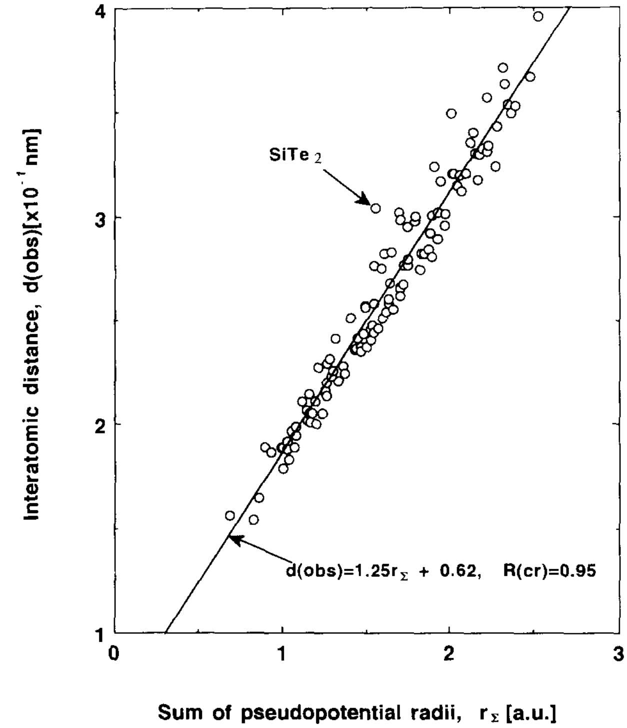

Fig. 2. The observed interatomic distance of sp-bonded closed-shell compounds as a function of the sum of weighted average pseudopotential radii.

calculated and observed interatomic distances respectively. The linear correlation coefficient obtained from 117 closed-shell sp-bonded compounds is 0.95 and the values of slope and intercept on the ordinate are 1.25 and 0.62 respectively.

Somewhat large positive deviations are obtained for some pnictides of Group IIIa elements and chalcogenides of heavier Group IIa elements. Halides of Group IIIa elements, except the fluorides, are not considered in this study because these halides in the solid state have a molecular character (for example, dimer for $AlBr_3$) and interatomic distances are only known for some halides. However, it should be noted that the experimental interatomic distances for molecular halides fit closely to the linear correlation for sp-bonded substances.

3.2. Open-shell sp-bonded compounds

The reproducibility of the linear correlation shown in Fig. 1 was examined for 66 open-shell sp-bonded compounds. In most cases, several interatomic distances are observed in an open-shell sp-bonded compound, so the interatomic distance was calculated by averaging the interatomic distances of respective bonds. In some compounds with molecular character, a few interatomic distances are shorter. In such cases, the interatomic distance of the compound is determined by averaging these shorter interatomic distances. The interatomic distances of these 66 open-shell sp-bonded compounds are given in Table 3, in which sums of pseudopotential radii are also listed. All these data are taken from structural reports [20] except for the three CsCl-type thallium halides; these data are from Ref. [19]. The resulting correlation of interatomic distance with the sum of the weighted pseudo-

Table 3

Data of interatomic distances d(obs), sums r_Σ of the pseudopotential radii and selected bond modes (BM) of cationic atoms for open-shell sp-bonded compounds

	d(obs)	r_Σ	BM		d(obs)	r_Σ	BM		d(obs)	r_Σ	BM
TlF	2.88	1.40_2	p	AsS	2.304	1.29_8	p	$AsBr_3$	2.36	1.35_4	p
TlCl	3.32	1.72_7	p	TlS	2.59[a]	1.63_6	sp	AsI_3	2.591	1.55_4	p
TlBr	3.44	1.82_9	p	TlTe	3.528	1.93_3	sp	SbF_3	2.27	1.11_7	p
TlI	3.636	2.02_9	p	PbO	2.351	1.34_5	p	$SbCl_3$	2.359	1.44_2	p
NaS	2.90	1.65_3	s	PbS	2.967	1.68_3	p	$SbBr_3$	2.503	1.54_4	p
NaSe	3.01	1.75_2	s	PbSe	3.064	1.78_2	p	SbI_3	2.765[a]	1.74_4	p
KS	3.22	2.09_3	s	PbTe	3.231	1.98_0	p	$BiCl_3$	2.500[a]	1.42_7	p
SiP	2.269	1.33_4	sp	BiI	3.14	1.88_6	p	$BiBr_3$	2.665[a]	1.68_6	p
GaS	2.334	1.37_1	sp	BiSe	3.00	1.72_9	p	BiI_3	3.07	1.88_6	p
GaSe	2.453	1.47_0	sp	BiTe	3.24	1.92_7	p	As_2O_3	1.77	0.96_9	p
GaTe	2.67	1.68_8	sp	$GaCl_2$	2.18[a]	1.32_5	sp	As_2S_3	2.283[a]	1.29_8	p
GeS	2.441	1.39_3	p	$GaBr_2$	2.33[a]	1.42_7	sp	As_2Se_3	2.421[a]	1.39_7	p
GeSe	2.58	1.49_2	p	GeF_2	2.00[a]	1.02_2	p	As_2Te_3	2.86[a]	1.59_5	p
GeP	2.625	1.40_4	sp	$GeBr_2$	2.57[a]	1.44_9	p	Sb_2O_3	1.977	1.15_0	p
GeAs	2.753	1.49_5	sp	$InBr_2$	2.50[a]	1.60_4	sp	Sb_2S_3	2.75[a]	1.48_8	p
InBr	2.80[a]	1.71_9	p	SnF_2	2.17[a]	1.18_2	p	Sb_2Se_3	2.703[a]	1.58_7	p
InS	2.57	1.55_0	sp	$SnCl_2$	2.72[a]	1.50_7	p	Sb_2Te_3	3.074	1.78_5	p
InSe	2.63	1.64_9	sp	PbF_2	2.52[a]	1.31_2	p	Bi_2O_3	2.38	1.29_2	p
InTe	2.819	1.84_7	sp	$PbCl_2$	2.98[a]	1.63_7	p	Bi_2S_3	2.67[a]	1.63_0	p
SnO	2.23	1.21_5	p	TeO_2	1.993	1.06_5	sp	Bi_2Se_3	2.98	1.72_9	p
SnS	2.64[a]	1.55_3	p	AsF_3	1.71[a]	0.92_7	p	Bi_2Te_3	3.145	1.92_7	p
SnSe	2.91[a]	1.65_2	p	$AsCl_3$	2.16[a]	1.25_2	p	Sn_2S_3	2.551[a]	1.49_3	p

TlCl, TlBr, TlI from Ref. [19], all other compounds Ref. [20].

[a] The average of the shorter bonds is taken as the interatomic distance by considering the anion's valence and number and, in some compounds with chain or ribbon structure, the average of the bonds related to the structures is taken as the interatomic distance.

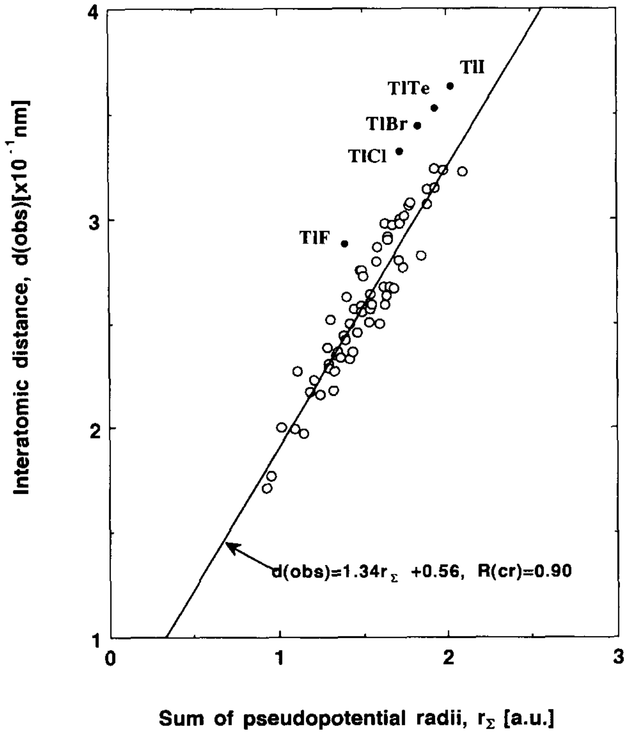

Fig. 3. The observed interatomic distance of sp-bonded open-shell compounds as a function of the sum of weighted average pseudopotential radii.

potential radii of constituent atoms is shown in Fig. 3. The plots of 62 compounds, except for five thallium compounds, fit closely to the straight line determined for sp-bonded elemental substances. However, the correlation for open-shell sp-bonded compounds is somewhat worse than that for closed-shell sp-bonded compounds, yielding a correlation coefficient of 0.90 for open-shell sp-bonded compounds.

Bonding modes for open-shell sp-bonded compounds, which are given in Table 3, are determined using two assumptions: (a) the anionic atom in the compound takes the sp bonding mode, and (b) the cationic atom in the compound takes the sp bonding mode, if the sum of valence electrons of cationic and anionic atoms in the compound is less than eight, and it takes the p bonding mode if the sum is more than nine. Assumption (b) corresponds to whether the s electrons are involved in the bonding or not.

4. Effective pseudopotential radii and bond characters for transition and lanthanide elements

In order to determine the bond characters of transition (TM) and lanthanide (LN) elements, as a first step we tried to evaluate the effective pseudopotential radii for these elements. In the present study, it is assumed that the effective pseudopotential radii of TM and LN elements satisfy the linear correlation between the sum of weighted average pseudopotential radii and interatomic distances for elemental substances. Justification of this assumption is discussed later by comparing the results derived. Hence, to zeroth approximation, it is permitted to extend this assumption to TM and LN compounds. Furthermore, for simplicity, the bond characters of TM and LN elements are approximated by the ratio of sd hybridization. For the compounds of LN elements, the substantial effect of 4f electrons is evaluated through sd hybridization. If these assumptions are permitted, the effective pseudopotential radii of TM and LN elements can be calculated by fitting the observed interatomic distances of these elemental substances to the linear correlation given in Fig. 1. The observed interatomic distances of TM and LN elemental substances are quoted from Ref. [18]. The numerical values of effective pseudopotential radii of TM and LN elements are given in Tables 4 and 5.

Subsequently, the ratios of sd hybridizations (R(sd)) for TM and LN elements are determined using the s, p and d pseudopotential radii of Zunger [14] for respective elements from the following equation:

$$R(\mathrm{sd})\,[\%] = \frac{r_{\mathrm{ps}}(\mathrm{eff}) - r_{\mathrm{sp}}}{r_{\mathrm{sd}} - r_{\mathrm{sp}}}\,100 \qquad (1)$$

Table 4
Effective pseudopotential radii r_Σ(eff), the ratios of sd hybridization R(sd), interatomic distances and ratios of d valence electrons for transition elements

Element	r_{ps}(eff) (AU)	R(sd) (%)	d(obs) (Å)	$10^2Q_\mathrm{d}/(Q_\mathrm{sp}+Q_\mathrm{d})$ (%)
Sc	1.00_1	$61._3$	3.212	60.0
Ti	0.88_1	$71._1$	2.896	67.5
V	0.77_7	$89._8$	2.622	78.0
Cr	0.73_0	$87._5$	2.498	78.3
Mn	0.81_9	$58._2$	2.731	–
Fe	0.72_4	$70._4$	2.482	82.5
Co	0.73_3	$62._2$	2.506	84.4
Ni	0.72_8	$70._7$	2.492	87.0
Cu	0.75_2	$56._8$	2.556	97.0
Zn	0.79_5	$32._8$	2.669	–
Y	1.12_9	$65._6$	3.551	50.0
Zr	0.98_8	$83._3$	3.179	67.5
Nb	0.86_7	$100._6$	2.858	80.0
Mo	0.81_6	$107._7$	2.725	80.0
Tc	0.80_8	$100._0$	2.703	–
Ru	0.78_8	$102._0$	2.650	–
Rh	0.80_3	$92._3$	2.690	85.6
Pd	0.82_6	$82._3$	2.751	91.0
Ag	0.87_9	$65._3$	2.889	88.2
Cd	0.91_2	$45._6$	2.979	–
La	1.21_2	$79._0$	3.770	–
Hf	0.96_9	$99._2$	3.127	–
Ta	0.86_7	$113._1$	2.86	80.0
W	0.82_2	$117._9$	2.741	78.3
Re	0.82_2	$112._1$	2.741	–
Os	0.79_8	$112._6$	2.675	–
Ir	0.81_2	$106._6$	2.714	77.8
Pt	0.82_4	$110._7$	2.746	80.0
Au	0.87_7	$94._2$	2.884	88.0
Hg	0.92_2	$65._5$	3.005	–

r_{ps}(eff) and d(obs) are given in atomic units and 10^{-1} nm (Å) respectively.

Q_d and Q_sp are the numbers of d and sp valence electrons reported by Nieminen and Hodges [23].

Table 5
Effective pseudopotential radii and the ratios of sd hybridization for lanthanide elements

Element	r_{ps}(eff) (AU)	R(sd) (%)	r_{sp} (AU)	r_{sd} (AU)	d(obs) (Å)
La	1.21_2	$79._0$	1.54_0	1.12_5	3.770
Ce	1.16_6	$87._6$	1.53_4	1.11_4	3.649
Pr	1.17_5	$83._3$	1.52_8	1.10_4	3.673
Nd	1.16_9	$82._3$	1.52_3	1.09_3	3.656
Pm	–	–	1.51_7	1.08_3	–
Sm	1.15_6	$80._9$	1.51_1	1.07_2	3.621
Eu	1.28_6	$49._4$	1.50_6	1.06_1	3.965
Gd	1.16_0	$75._6$	1.50_0	1.05_0	3.632
Tb	1.14_7	$76._5$	1.49_5	1.04_0	3.599
Dy	1.14_5	$74._8$	1.48_9	1.02_9	3.592
Ho	1.13_9	$74._0$	1.48_3	1.01_8	3.576
Er	1.13_2	$73._6$	1.47_8	1.00_8	3.559
Tm	1.12_4	$73._3$	1.47_2	0.99_7	3.537
Yb	1.25_2	$44._6$	1.46_5	0.98_6	3.876
Lu	1.11_2	$72._0$	1.46_1	0.97_6	3.505

where r_{sp} and r_{sd} are pseudopotential radii which are the arithmetical averages of s and p pseudopotential radii of Zunger, and of s and d radii respectively. r_{ps}(eff) is the effective pseudopotential radius determined from the observed interatomic distance and the linear correlation for sp-bonded elemental substances given in Fig. 1. Because numerical values of r_{sp} and r_{sd} have not been determined for lanthanide elements, except for La, they are evaluated using the values of s, p and d pseudopotential radii which are linearly interpolated from those of La and Hf.

Numerical values of sd hybridization ratios for TM and LN elements are given in Tables 4 and 5. As expected, there is a smaller contribution of sd hybridization in early TM elements such as the $(nd)^3$ configuration (Sc and Y) and post TM elements such as Cu, Zn and Cd, except for Au. With increasing atomic number in the same row, the effect of sd hybridization increases first, reaches a maximum, and then decreases. In the 3d series, however, the decrease in sd hybridization effect is not as large as for the late TM elements. It can be seen that the effects for 4d and 5d TM elements are larger than those for 3d elements. However, it is found that the effect of sd hybridization including the effect of 4f electrons is fairly strong for LN elements except for Eu and Yb. Although Sc and Y are included as rare-earth elements, their bond characters may be somewhat different from those of the lanthanides.

In order to justify the use of the effective pseudopotential radii for TM and LN elements, the reproducibility of interatomic distances for TM and LN compounds is evaluated using the empirical equation $d(\text{obs}) = 1.32r_\Sigma + 0.57$ given for sp-bonded elemental substances. In the present study, only interatomic distances for TM and LN compounds with B1 (NaCl) and B2 (CsCl) crystal structures are examined. Data for the interatomic distances of 101 TM compounds including Sc and Y and of 242 LN compounds are available [19,21]. The dependence of the interatomic distance on the sum of pseudopotential radii for these compounds is shown in Figs. 4 and 5. Highly linear correlations are obtained for both TM and LN compounds except for some LN compounds. The interatomic distances of almost all TM and LN compounds, except for some Tl and Bi compounds and a few TM nitrides, can be reproduced within 10% accuracy. However, the slopes of these linear correlations are considerably less than that (1.32) of the relation for sp-bonded elemental substances. The smaller slopes are attributed to the large positive deviations in several compounds with large interatomic distances and large negative deviations in some TM nitrides.

Finally, it should be noted that interatomic distances of Ag halides and chalcogenides of late 3d TM elements were not calculated using the effective pseudopotential radii in Table 4 but using the average values of s and p pseudopotential radii, neglecting the effect of sd hybridization. Chalcogenides of Cd are also plotted in Fig. 4 although these compounds which have B1 structure except for CdO are high pressure phases. The observed interatomic distance for CdO can be fitted to the calculated distance if it is calculated in the same way as for the Ag halides. Thus, in the compounds of 3d late- and post-TM elements, the effect of sd hybridization seems to depend on the chemical character (for example, electronegativity) of the partner element.

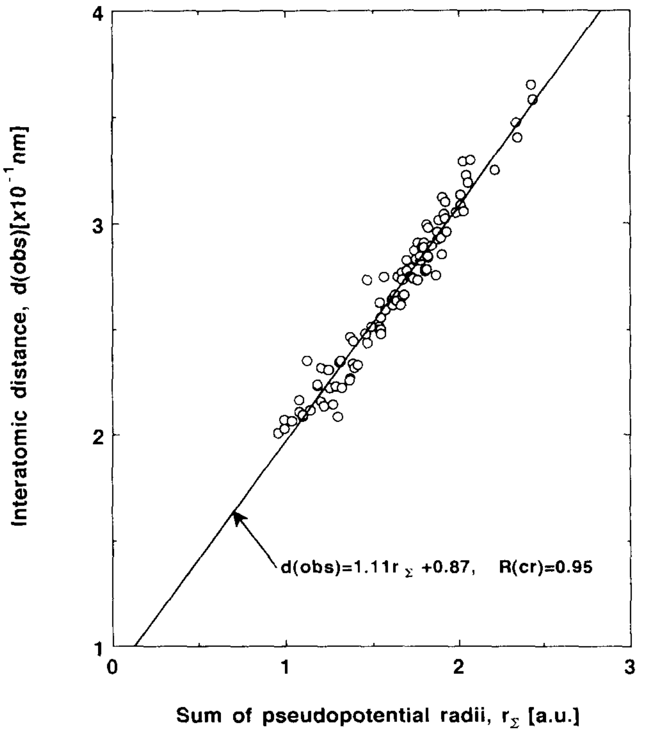

Fig. 4. The observed interatomic distance as a function of the sum of pseudopotential radii for transition metal compounds with B1 and B2 crystal structures. For transition elements, each effective pseudopotential radius is used for calculation of the sum of pseudopotential radii.

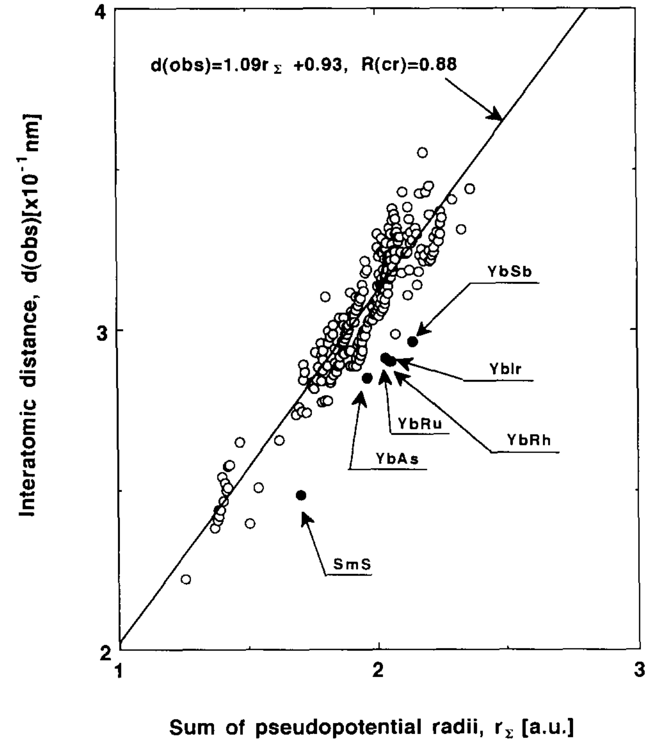

Fig. 5. The observed interatomic distance as a function of the sum of pseudopotential radii for lanthanide compounds with B1 and B2 crystal structures. For lanthanide elements, each effective pseudopotential radius is used for calculation of the sum of pseudopotential radii.

5. Discussion

It is found that a simple sp-bonding scheme yields a linear correlation between interatomic distances and the sums of average pseudopotential radii for sp-bonded elemental substances. In the simple sp-bonding scheme, the average pseudopotential radius for each sp-element is determined by weighting s and p pseudopotential radii, considering the electronic configuration of the atomic state. Based on the linear correlation, it is also indicated that interatomic distances for various closed- and open-shell sp-bonded compounds can be calculated within 10% accuracy. Thus, these results prove that, to zeroth approximation, the weighted average pseudopotential radius can be taken as the characteristic parameter for each element.

When the arithmetic average of s and p pseudopotential radii is used instead of the weighted average, we can obtain a similar linear correlation between the interatomic distance and the sum of the arithmetically averaged pseudopotential radii for 28 elemental substances. The linearity of the correlation based on the arithmetically averaged pseudopotential radii is similar to that based on the weighted averages because the correlation coefficient is 0.98 (see Section 2 and Fig. 1). However, this way of averaging has a worse influence on the deviation of calculated interatomic distances from the observed values for several fluorides, oxides and nitrides. As given in Table 6, the use of weighted average pseudopotential radii gives a better fit for 14 compounds such as AlN, Ga_2O_3 and InF_3, whereas the use of arithmetically averaged radii makes the fit better for nine compounds. Among 118 closed-shell sp-bonded compounds, the use of the weighted average pseudopotential radii gives a better fit for 71 compounds. Thus, the weighted average pseudopotential radii are more suitable than the arithmetically averaged radii for calculating the interatomic distance of sp-bonded compounds.

The slope of the linear correlation for elemental substances is slightly steeper than that for closed-shell sp-bonded compounds. Furthermore, the discrepancy between the two linear correlations increases with increasing interatomic distance. This discrepancy may be due to the variability of the atomic size of the heavier alkaline and alkaline-earth elements such as K and Sr, resulting in somewhat large positive deviations for the calculated interatomic distances of compounds of these elements. These deviations are probably due to differences in d electron contributions in elemental and compound states.

Fig. 6 shows the distribution of the number of compounds against the deviation of the calculated interatomic distance. A maximum is observed on the side of positive deviation. The asymmetrical distribution is mainly due to the positive deviations for the compounds of heavier alkaline and alkaline-earth elements and of Group III elements. As described above, the positive deviations for the compounds of heavier alkaline and alkaline-earth elements may arise from variability of the constriction effect due to d electrons. However, the positive deviations of the calculated interatomic distances for chalcogenides and pnictides of trivalent cations such as Al and Ga could not originate in the difference in d electron

Table 6
Several compounds for which the deviation values change largely when arithmetic average pseudopotential radii are used instead of weighted average radii

	Dev(WA) (%)	Dev(AM) (%)		Dev(WA) (%)	Dev(AM) (%)		Dev(WA) (%)	Dev(AM) (%)		Dev(WA) (%)	Dev(AM) (%)
NaF	−2.1	0.0	BN	−6.3	−4.9	BeO	2.9	6.1	Na_2O	−4.5	−2.6
MgF_2	0.5	3.1	AlN	4.8	8.1	MgO	−3.1	−0.7	SiO_2	−4.4	−1.3
AlF_3	4.9	9.0	GaN	2.3	6.2	Al_2O_3	0.5	4.6	GeO_2	−0.4	−2.4
GaF_3	0.0	4.8	InN	3.3	6.4	Ga_2O_3	5.4	9.6	SnO_2	1.9	3.0
InF_3	3.4	7.3	Be_3N_2	−7.7	−4.8	In_2O_3	−4.6	−0.8	PbO_2	3.1	5.1
TlF_3	−2.2	1.9	Mg_3N_2	−2.0	−0.0	Tl_2O_3	1.0	4.6			

Dev(WA) and Dev(AM) show the deviations for the usages of weighted and arithmetic average pseudopotential radii respectively.

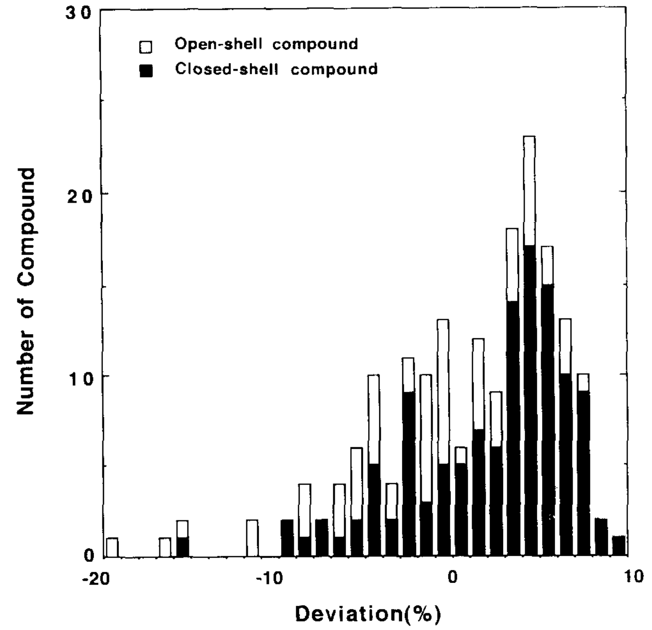

Fig. 6. Distribution of the number of compounds against the deviation of the calculated interatomic distance from the observed distance, $[d(\text{cal}) - d(\text{obs})]/d(\text{cal})$.

contribution but rather are due to the covalent effect. Plotting the deviations of the calculated interatomic distances for these compounds against $d(\text{cal})^{-2.5}$ (where $d(\text{cal})$ is the calculated interatomic distance), a linear correlation is obtained for these compounds with few exceptions, as shown in Fig. 7. Most chalcogenides of Group IV elements such as Si and Ge also satisfy the linear correlation. Since the covalent band gap is proportional to $d^{-2.5}$ and covalency can be defined using the covalent band gap [8], it is concluded that the deviation of the calculated interatomic distance from the observed value has a linear dependence on covalency, though limited to highly covalent compounds. Some compounds of In, Sn and Tl may be plotted on another straight line with steeper slope. The reason is not clear but is probably due to additional contributions of d electrons from the cations.

According to Zhang et al. [22], interatomic distances of diatomic crystals can be determined from the atomic s pseudopotential radii. In their approach, the effect of electronegativity difference is also considered for calculating interatomic distances. Excellent agreement with the observed interatomic distances has been obtained for compounds with B3 and B4 structures. The excellent agreement for B3 and B4 type compounds indicates that variability of atomic size can be corrected using the electronegativity difference, so that the correction based on the electronegativity difference corresponds physically to the observation of a good dependence of the deviation in this study on $d(\text{cal})^{-2.5}$. For B1 and B2 compounds, a good empirical relation between the interatomic distance and s pseudopotential radius has also been reported by Zhang et al. [22] but the agreement is not as excellent as for the compounds of B3 and B4 structures even though the correction is applied using the electronegativity differences. The less excellent agreement for B1 and B2 type compounds coincides with the lack of good dependence of the value of deviation on the calculated interatomic distance in this study. This lack of dependence of the deviation from the observed interatomic distance may be due to the difference in bonding modes of light $(ns)^N$ ($N = 1$ or 2) elements in the compound state from those in the atomic state. For these elements, it may be necessary to consider some p-character for their bonding modes in the compound state. For example, the bonding modes of Li and Mg change with the kind of anionic partner atom, resulting in the occurrence of both positive and negative deviations from the observed interatomic distances.

It can be expected that the interatomic distances of compounds can also be obtained from the experimental atomic radii determined from experimental interatomic distances for elemental substances (see Table 1), instead of the average pseudopotential radii. When the interatomic distances of sp-bonded compounds (given in Table 2) are calculated from the values of experimental interatomic distances (given in Table 1), a linear correlation is also obtained, as shown in Fig. 8. However, the correlation coefficient (0.93) is somewhat worse than that (0.95) for the results in Fig. 2 and the scatter of data points in Fig. 8 is clearly wider than that in Fig. 2. The wider scatter may be owing to the fact that determination of each atomic radius from the experimental interatomic distance is influenced by the difference in bond character in each elemental substance. For example, atomic

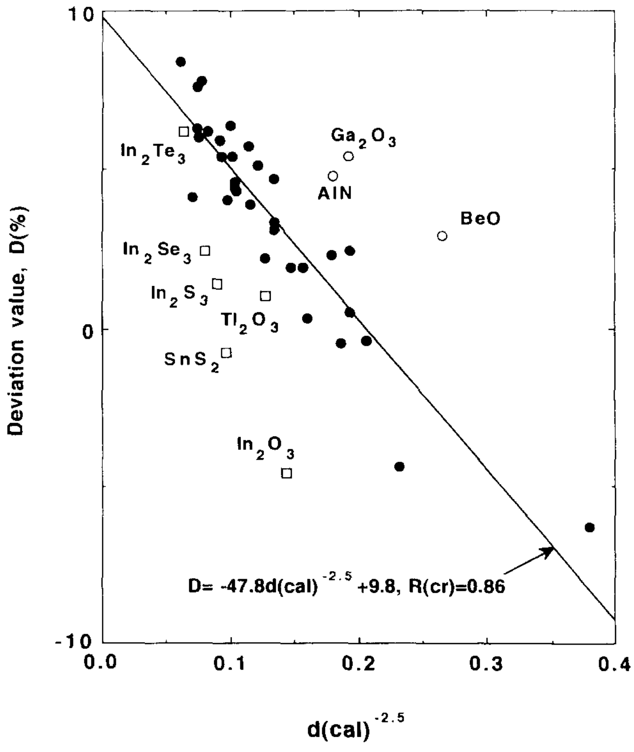

Fig. 7. The deviation of the calculated interatomic distance as a function of $[d(\text{cal})]^{-2.5}$ for chalcogenides and pnictides of trivalent and tetravalent cations.

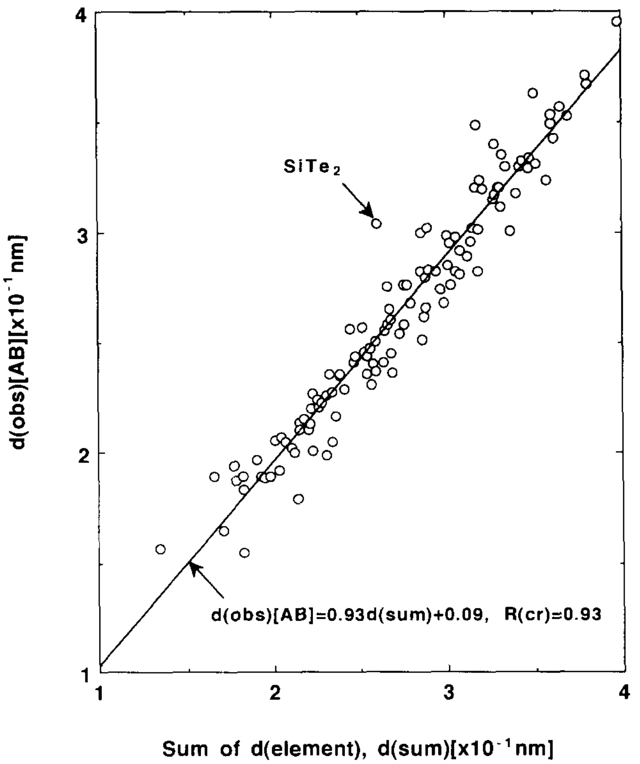

Fig. 8. Correlation between the observed interatomic distance d(obs) [AB] of closed-shell sp-bonded compounds and the interatomic distance d(element) calculated from the experimental atomic radii, which correspond to the half values of the experimental interatomic distances for elemental substances.

radii for metallic substances such as Na, Ca and Al are calculated using metallic interatomic distances, while those for molecular substances such as H_2, O_2 and N_2 are calculated from covalent interatomic distances. However, calculation of interatomic distances through the pseudopotential radii is based on the atomic state, so that these atomic radii are independent of bond character. Although not clearly explainable, it is shown that the use of pseudopotential radii yields a better fit in the calculation of interatomic distances of compounds.

For the open-shell sp-bonded compounds, precise determination of interatomic distances depends on selection of the bonding mode. In the present study, it is simply assumed that the anionic atom in a compound takes the sp-bonding mode and the cationic atom in the compound takes sp- or p-bonding modes, depending on the number of total valence electrons in the compound. This simple assumption is not always satisfied because p electrons may not ideally contribute to sp-bonding and p-bonding may occur in a compound with a total number of valence electrons less than eight. However, as shown in Fig. 3, the two simple assumptions taken in Section 3.2 are not so unsuitable for determination of the bonding mode for open-shell sp-bonded compounds, except for some thallium compounds, because these assumptions yield a highly linear correlation between the observed interatomic distances and sums of the weighted average pseudopotential radii. Thallium compounds are quite singular and the large deviations of these calculated interatomic distances remain unclear.

The most interesting point for TM and LN elements is whether the effective pseudopotential radii for these elements can be determined by fitting the observed interatomic distances of these elemental substances to the correlation given by the empirical equation $d(\mathrm{cal}) = 1.32r_{\Sigma} + 0.57$. The correctness of these effective pseudopotential radii cannot be examined directly because no data related to these radii are available. However, an indirect argument can be derived from the ratio of the number of sp electrons to the number of d electrons because the ratio can be compared roughly with the sd hybridization ratio. The ratios for TM metals are calculated from previous results of Nieminen and Hodges [23]. Numerical values are shown in Table 4. Comparing these values with sd hybridization ratios for TM elements, these sd hybridization ratios are not so unreasonable except for post-transition metals. In particular, sd hybridization ratios for early TM elements show fairly good agreement with the ratios of electron numbers. The ratios of sd hybridization for 4d and 5d TM elements calculated from pseudopotential radii may be overestimated. Unfortunately, sd hybridization ratios for LN elements cannot be discussed because no data are available. Consequently, the ratios of sd hybridization for TM and LN elements are suggested as given in Table 3 but these numerical values must be confirmed by examining their suitability for the construction of crystal structure maps and prediction of various physicochemical properties such as heat of formation or melting point.

Lastly it should be noted that relativistic effects may be taken into account for the pseudopotential radii of heavier elements. According to Zhang et al. [24], the relativistic effect increases with increasing atomic number of the element, and the maximum differences between relativistic and non-relativistic pseudopotential radii reach about 10%, so that the relativistic effects may be considered to cause the deviations of the calculated interatomic distance in the present study.

6. Summary

The interatomic distances of 178 closed- and open-shell sp-bonded compounds can be calculated within 10% accuracy from the weighted average pseudopotential radii of the 28 sp-bonded elements, which are determined by Zunger's pseudopotential radii on the basis of the sp-bonding scheme and outermost electron configuration. It is suggested that deviation of the calculated interatomic distances arises from the effect covalency and variability of atomic size in the compounds owing to the difference in d electron contribution and some p-character in light $(ns)^N$ elements. Interatomic distances for most of 101 transition metal and 242 lanthanide compounds are calculated within 10% accuracy using the effective pseudopotential radii of transition elements and lanthanide elements. These are determined by assuming that the linear correlation for sp-elemental substances is valid for transition elements and lanthanide elements too. Furthermore, it is suggested that the contributions of d electrons to the bondings in transition elements and lanthanide elements can be evaluated numerically from the empirical linear correlation for sp-bonded elemental substances and the sd hybridization scheme.

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