Estimation of bonding character of lanthanide by interatomic distance and pseudopotential radius

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Abstract

A new parameter ($d(eq/B)$) consisting of the observed interatomic distance ($d(obs)$) and angular momentum quantum number (ℓ) was proposed for the purpose of expressing bulk modulus by a single-valued function. Bonding character (d character) of both lanthanide and transition metal(TM) elemental substances was estimated by determining numerical value of ℓ so as to fit experimental bulk modulus to the value calculated from an empirical formula of bulk modulus (B); $B = k[d(eq/B)]^{-3.5}(k = 571)$, where $d(eq/B)$ named "equivalent interatomic distance" is defined by $d(obs)/\sqrt{\ell(\ell + 1)}$. The empirical formula was determined from the data of sp^3-bonded elemental substances (C(d), Si, Ge and Sn(w)), Re and Os under the assumption that the angular momentum quantum numbers for the sp^3-bonded and two TM elemental substances are given by $\ell = 1$ and $\ell = 2$, respectively. It was indicated that the value of d character for lanthanide except Eu and Yb ranges between 54% ($\ell = 1.08$) and 63% ($\ell = 1.26$) under the condition of neglecting the effect of p electrons. A lower d character than 50% was shown in Eu and Yb. TM elemental substance showed a widely ranged d character from about 100% ($\ell = 1.998$) to 60% ($\ell = 1.20$), depending on the period and group. Rare-earth metals and II-b post-TM showed somewhat lower value of d character than 60%.

Good correlation between s-orbital electronegativity of Zunger and $d(eq/B)$ suggests that $d(eq/B)$ almost corresponds to the inverse of the electronegativity of s electron though some deviation was observed in the 4d and 5d TM elemental substances. Excellent correlation was observed between $d(eq/B)$ and surface tension at melting point for elemental substances, indicating further application of $d(eq/B)$ to other physical and chemical properties.
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1. Introduction

Up to the present time, the importance of interatomic distance in crystalline materials has been underlined in the context of atomic and ionic radii [1–5] as well as in the expression of bond character [6–8]. According to Van Vechten [6] and Phillips [7], the interatomic distance is related with the covalency (or ionicity) of $A^N B^{8-N}$ octet compounds. Further, covalent band gap (E_h) of the compound can be estimated using the formula $E_h = 40d^{-2.5}$, where d is the interatomic distance for A–B bond in the AB compound [7]. The relation between E_h and d was applied to the estimation of bulk modulus and possibility of superhard carbon nitride was

suggested from the bulk modulus predicted by interatomic distance through the empirical formula on the tetrahedral AB compounds [9,10]. The relation between bulk modulus and interatomic distance was extended to various compounds on the basis of the power functional formula [11,12], and it has indicated that the approach is available for the understanding of hard materials [13].

Instead of the interatomic distance, the pseudopotential radius has been proposed as a universal parameter for describing the chemical characters of atom in compound and successful results have been obtained in structural mapping of compounds [14–17]. Further, the pseudopotential radius can be related to the elecronegativity [14,18] and the interatomic distance in AB compounds with a few fundamental structures [19]. Based on these previous results, the author

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attempted to describe the bonding character of binary compounds using Zunger's pseudopotential radius [17], combined with the concept of bond orbital model [20] and a successful result on the band gap and ionicity for binary compounds has been obtained using the band parameters, which were constructed by pseudopotential radius [13,21]. Further, a structural map for AB compounds with several fundamental structures has been successfully constructed by selecting the band parameters as the coordinates [13,21–23].

Structure and bonding of elemental substances have been performed by many approaches [24,25]. Especially, electronic structures of elemental substances including f-shell metals have been well investigated and connected with mechanical properties, such as bulk modulus and Poisson ratio [26,27]. However, simply available parameters for describing physical and chemical properties of transition metal (TM) and lanthanides have not well determined. In the present study, atomic character of lanthanide as well as TM in elemental substance was attempted to describe using the interatomic distance and pseudopotential radius. Attempt to estimate bonding character of both lanthanide and TM elemental substances was performed using dependence of bulk modulus on the interatomic distance. Further, d characters of these elemental substances were estimated by introducing a new parameter consisting of interatomic and angular momentum quantum number.

2. Interatomic distance and bulk modulus

Interatomic distance is the important parameter in the semi-empirical prediction of superhard material because the prediction is made on the basis of the power functional relation between bulk modulus (B) and interatomic distance (d). We have reported that the relation between B and d can be expressed by power functional formula; $B = Cd^{-m}$ (C and m are the constants) and available for considering bonding character of compounds [7]. Though possibility to estimate bonding character is suggested from the relation between B and d, however, no successful description of bulk modulus by a single-valued function of interatomic distance has been proposed even in the elemental substances. In the previous approach [12], bulk modulus for elemental substances has been described by power functional formula, assuming a priori five bonding modes based on respective valence electron character. Further, it has indicated that the value of power increases with increasing the period number that respective elemental substance is placed in the periodic table. The increase of the power value suggests close relation of interatoimic distance to the angular momentum of binding electron. Accordingly, in the present study, description of bonding character of metallic and semi-conductive elemental substances including lanthanides is attempted by transforming the observed interatomic distance to a new interatomic distance including angular momentum effect.

Now we consider the method to transform the observed interatomic distance as follow. An elemental substance with a similar transformed interatomic distance should have a similar bulk modulus because bulk modulus is expressed by a single-valued function of the transformed interatomic distance. In the present study, C(d) (diamond) and Os with the first and second largest bulk modulus are taken as standard substances in order to transform the observed interatomic distance. In order to transform these interatomic distances so as to give a similar bulk modulus to these elemental substances, the ratio of interatomic distance of Os to that of C(d), that is, 1.731 becomes the transforming factor. The value almost equals $\sqrt{3}$ that corresponds to the ratio of eigenvalue ($\sqrt{6}$) of angular momentum for d electron to that ($\sqrt{2}$) for p electron. Therefore, $d(obs)/\sqrt{\ell(\ell+1)}$ is defined as the equivalent interatomic distance ($d(eq/B)$) in the present study. Examining the relation between $B(obs)$ and $d(eq/B)$ by taking $d(obs)/\sqrt{2}$ for sp-bonded elemental substances and $d(obs)/\sqrt{6}$ for nd and 4f elemental substances as the abscissa, we obtain Fig. 1. In this figure, the data for 3d elemental substances are not plotted for avoiding complexity and the power functional relation determined from four sp^3-bonded elements (C(d), Si, Ge and Sn(w)) and two 5d elements (Os and Re) is given by the straight line in log-log scale. The power value in the relation (called as fundamental relation) is 3.5 and shows an excellent agreement with the value for tetrahedrally-bonded AB-type compounds [9].

As shown in this figure, the plots for sp-bonded elemental substances are placed close to the fundamental relation except for alkaline elemental substances, which are placed in the underside of the fundamental relation. The plots for 4d and 5d elemental substances also deviate from the fundamental relation and are placed in the underside of its relation. Lanthanides are plotted on a curve (straight line in log–log
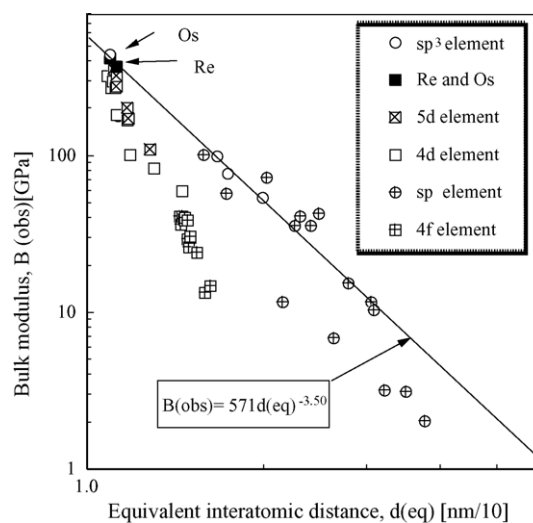

Fig. 1. Relation between bulk modulus (B(obs)) and equivalent interatomic distance in various elemental substances.(data for 3d elemental substances are omitted for simplicity. Definition of the equivalent interatomic distance is described in the text.).

scale) extrapolated from 4d and 5d elemental substances and these plots deviate further from the fundamental relation. Deviation from the fundamental relation is attributed to the assumption that angular momentum number can be taken as 1 for sp-bonded elemental substances or as 2 for nd and 4f elemental substances. Accordingly, deviation from the fundamental relation corresponds to decrease of angular momentum number, suggesting the contribution of s electron on bulk modulus. Especially, large contribution of s electron to bulk modulus is suggested from large deviation in lanthanides and 3d transition metal elements. Thus, *d* or *p* character of elemental substance can be determined under the assumption that the fundamental relation ($B = 571d(eq/B)^{-3.50}$) allows to describe bulk modulus of elemental substance and angular momentum effect can be contained in $d(eq/B)$ by replacing in the form of $d(obs)/\sqrt{\ell(\ell+1)}$. In the next section, the values of *d* character calculated from the above-described method is compared with those of sd(%) calculated previously under assumption of sd hybridization [26].

3. Effective angular momentum quantum number and *d* character of nd and 4f elemental substances

As indicated Section 1, the angular momentum quantum number ℓ satisfies the following formula under that assumption that $d(obs)$ is transformed into $\sqrt{\ell(\ell+1)}d(eq/B)$:

$$\ell(\ell+1) = [571/B(obs)]^7 d(obs)$$

Numerical value of ℓ can be estimated by solving the quadratic equation when $B(obs)$ and $d(obs)$ are known. Numerical values of ℓ for the elemental substances of fifth period are given in Fig. 2 as an example. In the 5d elemental substances, angular momentum quantum number changes remarkably from $\ell = 1.9$ (for Os) to $\ell = 0.9$ (for Hg). In the lanthanides, the value lies between 1.0 and 1.3 except for Eu and Yb. Eu and Yb take a ℓ value below 1.0 and close to that of
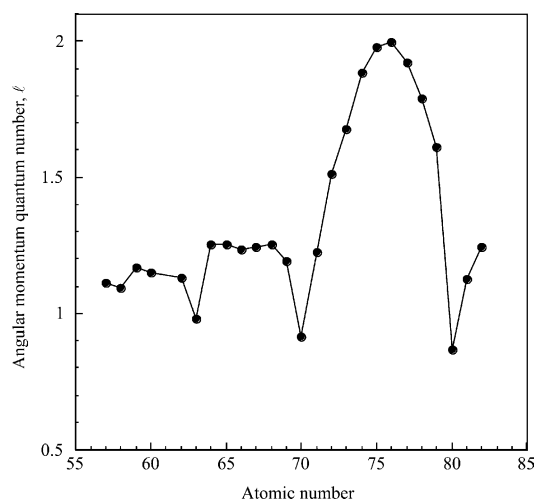
Ba. Assuming that bonding characters of nd and 4f elemental substances are mainly determined by s and d electrons and the effect of p electrons can be ignored, *d* character of these elemental substances can be estimated from ℓ value. Numerical values of *d* characters for nd elemental substances are given in Fig. 3. In the 3d elemental substances, a minimum is observed for Mn and most of 3d elemental substances show *d* character around 70%. In the 4d elemental substances, a maximum is observed for Tc and Ru and its value reaches about 90%, and a higher *d* character in 5d elemental substances is observed. Os shows the highest *d* character of about 100% that reflects the second highest bulk modulus.

Subsequently, *d* character estimated from $B(obs)$ and $d(eq/B)$ was compared with sd% value that was estimated from the relation between $d(obs)$ and pseudopotential radius, $r(ps)$ [28]. The result is shown in Fig. 4. Correlation between these physical factors is not so bad, so it is judged that these have almost same physical meaning. Except for Zn, a fairly good agreement is obtained in 3d and 4d early TM elemental substances. In the 5d TM elemental substances, however, *d* character obtained from $B(obs)$ show a lower value than that estimated from the relation between $d(obs)$ and $r(ps)$. Further, except for four elemental substances (Zn, Cd, Cu, Co), the values of *d* character estimated from $B(obs)$ are lower than those from relation between $d(obs)$ and $r(ps)$.

Lanthanides show larger discrepancy in between *d* character and sd% as shown in Fig. 5. The figure is illustrated in the same ordinate under the assumption that *d* character has the same physical meaning to sd%. Discrepancy in light lanthanides is larger than that in heavy ones. For Eu and Yb, these characters show an excellent agreement with each other. Though detailed reasons on the large discrepancy for lanthanides is unclear, the important reason is attributed to the fact that sd% is estimated by a linear relation

Fig. 2. Dependence of angular momentum quantum number (l) on the atomic number in the 5d and 4f elemental substances.
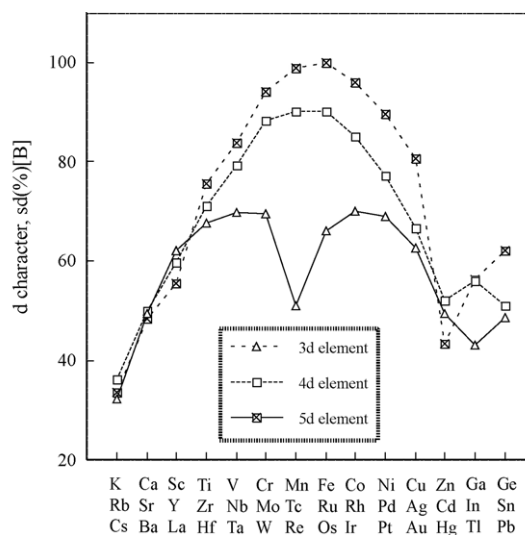

Fig. 3. Dependence of *d* character on the atomic number in the 3d, 4d and 5d elemental substances (data for some non-transition (sp-bonded) elemental substances are also shown).
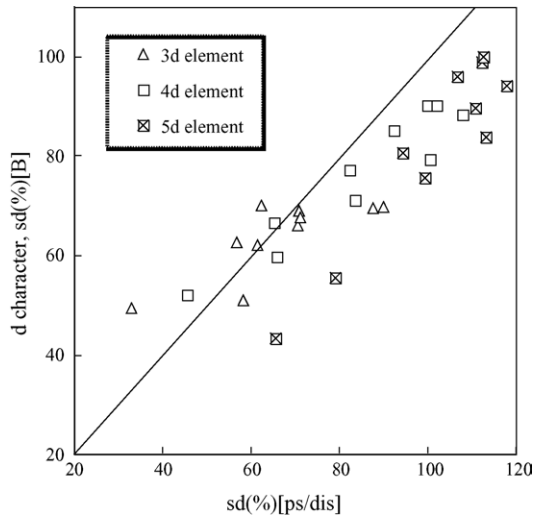
Fig. 4. Comparison of *d* character in the present study with the value of the sd% estimated from the relation between pseudopotential radius and observed interatomic distance.

between *d*(obs) and *r*(ps), whereas *d* character is estimated by a power function of *d*(obs) against *B*(obs). Further, electronic configuration for elemental substances has been assumed a priori in the approach based on the relation between *d*(obs) and *r*(ps).

The value of sd% can be verified by the numbers of valence electrons. Numbers of s-, p- and d-electrons in lanthanides have been calculated by various computational methods. According to the result by Freemen et al. [29], the number of d electron in the lanthanides except for Eu and Yb decreases with the increase of atomic number (from 1.93 for La to 1.44 for Lu), while the numbers of s- and p-electrons increase with increasing atomic number, respectively. Estimating the rough value of sd% for respective lanthanide from the average angular quantum number calculated by these electron numbers, the sd% value ranges from about 73% for La, through about 65%
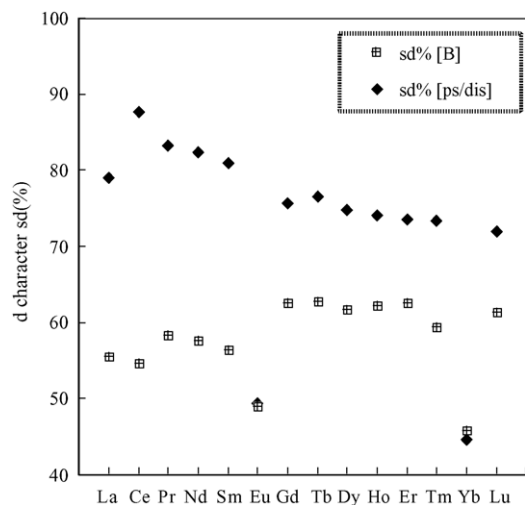
for Gd, to about 60% for Lu and decreases with the increase of atomic number. The values of sd% for heavy lanthanides show a good agreement with those estimated by the relation between *d*(eq/*B*) and bulk modulus. On the other hand, the values for light lanthanides are placed in between those estimated by two methods. Further, decrease of sd% value with atomic number in the computational method shows a similar tendency to the result estimated by the relation between *r*(ps) and interatomic distance. The values of sd% for Eu and Yb in the present study show an excellent agreement with the computational results. Thus, *d* character for heavy lanthanides estimated from *d*(eq/*B*) and bulk modulus can be supported by the computational result but some discrepancy is observed in light lanthanides.

4. Relation between equivalent interatomic distance and physical/chemical parameters

In this section, we consider physical and chemical meanings of *d*(eq/*B*) by comparing with some physical and chemical parameters. First, *d*(eq/*B*) is compared with electronegativity for the purpose of examining chemical activity of valence electrons in elemental substances. Until now, many scales have been proposed for electronegativity. In the present study, the electronegativity scale by Pauling is compared with *d*(eq/*B*) because Pauling's electronegativity, χ (Pauling), is one of the popular scale [30]. Relation between χ (Pauling) and *d*(eq/*B*) is shown in Fig. 6. A fairly good correlation is observed except for several sp-bonded elements (Pb, Tl, In and Sn), Hg and Au. Correlation of *d*(eq/*B*) to χ (Pauling) is excellent in lanthanides. As indicated above, a fairly large discrepancy is observed in the elemental substances that belong to the groups from 11 to 14. In these atoms, the completely-filled d shell exists inside of outermost valence s and/or p electrons. The completely-filled d shell in these atoms gives
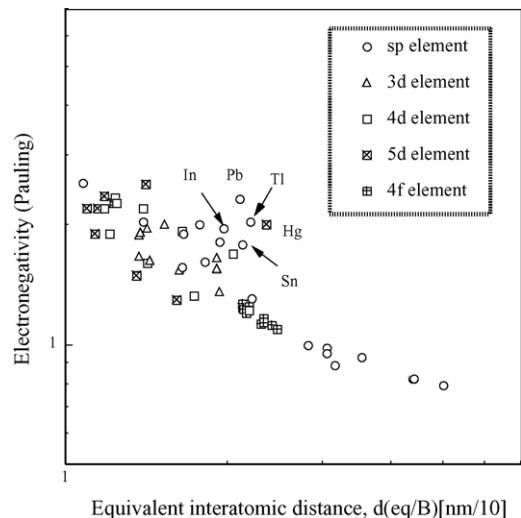

Fig. 5. Dependence of *d* character on the atomic number in lanthanide elemental substances.

Fig. 6. Correlation between equivalent interatomic distance (*d*(eq/*B*) and Pauling's electronegativity (χ (Pauling)) in elemental substances.
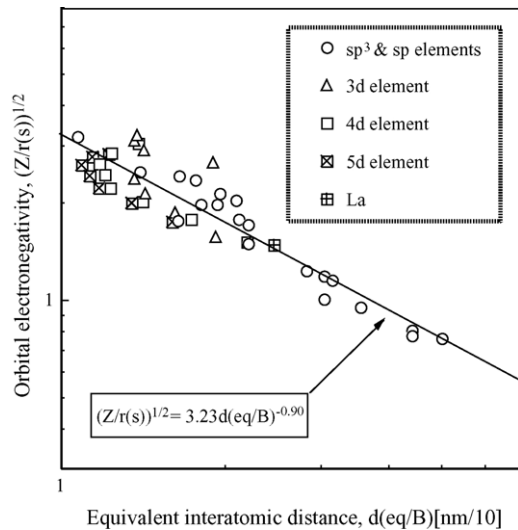
Fig. 7. Correlation between equivalent interatomic distance (d(eq/B) and Zunger's s-orbital electronegativity $[Z/r(s)]^{1/2}$ in elemental substances.

Fig. 8. Correlation between equivalent interatomic distance (d(eq/B) and surface tension at melting point in elemental substances.

a high shielding effect to the valence electrons. Accordingly, it is expected that electronegativity decreases with the increase of d(eq/B). However, these atoms still maintain high electronegativity irrespective of decreasing d(eq/B). These high electronegativities suggests strong interaction between s (or p) and d electrons irrespective that d shell is completely filled.

Subsequently, d(eq/B) is compared with the parameter, $[Z/r(s)]^{1/2}$, that is constructed from Zunger's pseudopotential radius of s electron because the parameter corresponds to the orbital electronegativity of s electron [18]. A good correlation between d(eq/B) and $[Z/r(s)]^{1/2}$ is obtained as shown in Fig. 7, though some scatter of plot is observed with increasing $[Z/r(s)]^{1/2}$. Pseudopotential radius of lanthanide was determined only for La and the plot is well placed on the curve of $[Z/r(s)]^{1/2}$ against d(eq/B). Accordingly, the orbital electronegativity of s electron for lanthanide can be estimated from the value of d(eq/B).

Further, we show an excellent dependence of surface tension against d(eq/B). Fig. 8 shows the dependence of surface tension (γ_m) at the melting point for 49 elemental substances against d(eq/B). Compared with the correlations for both χ (Pauling) and $[Z/r(s)]^{1/2}$, it is emphasized that γ_m can be defined by d(eq/B) very well. Until now, the estimation of surface tension (γ) for liquid metals has been performed by theoretical approaches based on the distribution function and free electron model and so on [31]. Relations between γ and the isothermal compressibility of liquid metal have been obtained from the approaches based on the hard sphere model and fluctuation theory. Accordingly, a correlation between γ and d(eq/B) is suggested because the compressibility corresponds to the reverse of bulk modulus. An expression of γ by atomic volume (V_m) has been also given in the approach based on a free electron model [31]. Therefore, a correlation between γ and interatomic distance is suggested though the
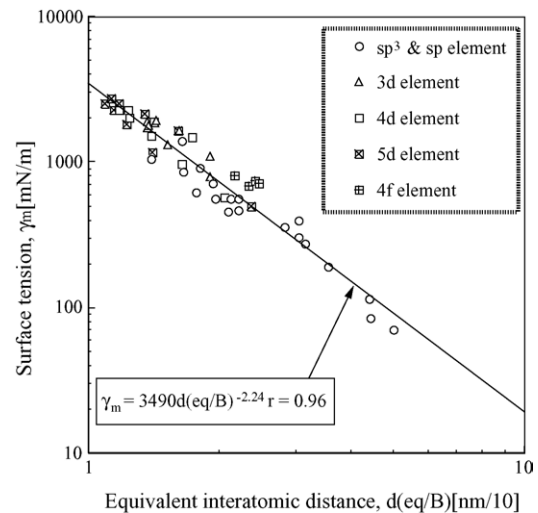
difference between interatomic distances in solid and liquid states should be taken into consideration. However, atomic volume does not give so good correlation to γ. Compared with the previous results, the excellent correlation is obtained between γ and d(eq/B) as shown in Fig. 8, indicating further application of d(eq/B) to other physical and chemical properties, though detailed understandings for the present result is desired in further investigation.

Lastly, we discuss shortly the assumption of hypothetical relation; d(eq/B) = d(obs)/$\sqrt{\ell(\ell+1)}$, from angular distribution of electrons. With increasing the value of ℓ, spatial distribution of electron becomes asymmetric and spreads to a particular direction, depending on the total angular momentum $\sqrt{\ell(\ell+1)}\hbar$. Thus, it is suggested that transformation of d(obs) to d(eq/B) by $\sqrt{\ell(\ell+1)}$ corresponds to the correction to reduce angular momentum effect. However, the average distance of electron in hydrogen-like atom consists of n- and l-dependent terms. Therefore, the simple correction based on $\sqrt{\ell(\ell+1)}$ may be crude approximation to reduce angular momentum effect even if the transformation is reasonable. Further, the reasonableness of the hypothetical relation should be considered in more details from both theoretical and empirical standpoints though excellent correlations to s-orbital electronegativity of Zunger and surface tension are indicated.

5. Summary

A new parameter, that is called "equivalent interatomic distance" (d(eq/B)) defined by d(obs)/$\sqrt{\ell(\ell+1)}$ (ℓ; angular momentum quantum number), was introduced in order to express bulk modulus by a single-valued function of interatomic distance. Fundamental power function ($B = k[d$(eq/B)$]^{-3.5}$) ($k = 571$)) between bulk modulus and d(eq/B) was determined from the data on sp^3-bonded

elemental substances(C(d), Si, Ge and Sn(w)), Re and Os by assuming that the values of ℓ for these substances are 1 and 2, respectively. The value of ℓ for other respective substance was determined from the observed bulk modulus so as to fit to the value calculated by the fundamental power function. The values of d character estimated from these calculated ℓ values were estimated to range between 54% ($\ell = 1.08$) and 63% ($\ell = 1.26$) for lanthanide elemental substances except for Eu and Yb under the condition of neglecting the effect of p electrons. A value of d character less than 50% was shown in Eu and Yb. TM elemental substance showed a widely ranged d character from about 100% ($\ell = 1.998$) to 60% ($\ell = 1.20$), depending on the period and group. Rare-earth metals and II-b post-TM showed somewhat lower value of d character than 60%.

The value of d character in the sd% scale for heavy lanthanides showed an good agreement with those estimated by computational method based on quantum mechanics, while these values for light lanthanides were somewhat lower than those by the computational method. Excellent agreement was obtained between these values for Eu and Yb.

Good correlation between s-orbital electronegativity of Zunger and $d(\text{eq}/B)$ was obtained, suggesting that $d(\text{eq}/B)$ almost corresponds to the inverse of the electronegativity of s electron though some deviation was observed in the 4d and 5d TM elemental substances. Excellent correlation was obtained between $d(\text{eq}/B)$ and surface tension at melting point for elemental substances, indicating further application of $d(\text{eq}/B)$ to other physical and chemical properties.

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