Understanding of Superconductivity in Elemental Substances by Pseudopotential Radii

Y. Makino and K. Yoshimura

Graduate School of Science, Kyoto University, Kitashirakawa Oiwake-cho, Sakyoku, Kyoto, 606-8502, Japan

E-mail: ymak@kuchem.kyoto-u.ac.jp

Abstract. Two dimensional map on superconductivity in elemental substances was constructed using pseudopotential radii and its derived parameter, $(Z/r(s))^{1/2}$, where $r(s)$ and $Z$ are the pseudopotential radius of s electron and valence. It is found that superconducting elements are well mapped by selecting the difference between pseudopotential radii and $(Z/r(s))^{1/2}$ as the coordinates. It is suggested that transition temperature($T_c$) of superconductivity is related to the $(Z/r(s))^{1/2}$ and the cube of $r(s)$ except several transition metals.

1. Introduction

Since the discovery of high $T_c$ cuprate superconductors[1], it has been continued to search the controlling factors of high $T_c$ and other new superconductors[2-4]. It has been indicated that electronegativity is a key chemical parameter for understanding superconductivity in both elemental substances and compounds[5,6]. For example, low-$T_c$ superconductors have a value of electronegativity ranging from 1.2 to 2.32 in Pauling’s scale and high-$T_c$ superconductors are plotted around a value of electronegativity( for example, 2.5 in Pauling’s scale)[7]. Similar results have been reported in the other approaches based on the electronegativity[8,9]. In these approaches, however, the relation between physical picture and electronegativity, which is a typical chemical parameter, has not been clarified well.

Pseudopotential radius is a physical parameter corresponding to the radius which pseudopotential for respective valence electron (that is, s, p or d electron) becomes zero in atomic system with many electrons[10] and has been applied to construct the crystal structural maps for compounds[11,12] and to phase designing of hard coatings[13,14]. Pseudopotential radius of s electron has been connected with the electronegativity and the orbital electronegativity for s electron through the formulae of $\chi(s)=k(Z/r(s))^{1/2}$[15], where $\chi(s)$:orbital electronegativity of s electron, $k$: constant, $Z$:valence, $r(s)$:pseudopotential radius of s electron. Thus, pseudopotential radius is the interesting parameter that can combine physical picture with chemical characters. In this study, it is aimed to construct a two dimensional map on the superconducting elemental substances by using the pseudopotential radius and
orbital electronegativity in order to understand superconductivity from chemical standpoint. Further, it is tried to describe transition temperature ($T_c$) in elemental substances by pseudopotential radius.

2. Selection of parameters

Pseudopotential radii calculated by Zunger are used in this study because the radii of s, p and d electrons for 70 elements are available[16]. Under the assumption that the electrons in the outermost Fermi surface contribute to superconductivity, the root of the valence divided by pseudopotential radius of s electron ($r(s)$), that is $(Z/r(s))^{1/2}$, is adopted as the abscissa in the two dimensional map. Differences between the pseudopotential radii of s electron and p electron or between s electron and d electron, that is $|r(s)-r(p)|$ or $|r(s)-r(d)|$, are taken as the ordinate. In this study, orbital electronegativity of s electron for respective element is approximately adopted by the value of $(Z/r(s))^{1/2}$. In order to examine the dependence of $T_c$ on the pseudopotential radius of s electron, it is assumed that s and p electrons contribute to superconductivity in so-called sp element and two s electrons simply contributes to superconductivity in transition metal. All data on $T_c$ are quoted from Ref.17.

3. Results and Discussion

Two dimensional map by taking $(Z/r(s))^{1/2}$ and $|r(s)-r(p)|$ (or $|r(s)-r(d)|$) as coordinates is shown in Fig.1. In this map, the data are plotted by distinguishing among superconductor(SC), metastable superconductor(meta-) and non-superconductor(non-SC). The values of $|r(s)-r(d)|$ are adopted as the ordinate values for three post-transition metals (that is, Cu, Ag and Au). As shown in this figure, decisive factor for superconductivity is the orbital electronegativity of s electron and the sp-bonded elemental superconductors are plotted between $(Z/r(s))^{1/2} \approx 1.3$ (lower limit) and $(Z/r(s))^{1/2} \approx 2.3$. In the transition metals, superconductivity appears beyond the threshold value of $(Z/r(s))^{1/2}$ in sp-bonded elemental substances and this may be due to d-band in the transition metals. The threshold value for superconductivity of transition metals in the larger $(Z/r(s))^{1/2}$ side decreases with increasing $(Z/r(s))^{1/2}$.

Figure 1. Two dimensional map on the superconductivity for elemental substances by taking $(Z/r(s))^{1/2}$ and $|r(s)-r(p)|$ (or $|r(s)-r(d)|$) as the ordinates. $(r(s), r(p)$ and $r(d)$ are the pseudopotential radii, respectively, and $Z$ is valence.)
Figure 2. Dependence of average band gap in elemental substances on the \((Z/r(s))^{1/2}\).

Figure 3. Relation between transition temperature \((T_c)\) and \((Z/r(s))^{1/2}\). (The values of \((Z/r(p))^{1/2}\) is used as corrected plots for La and \(T_c\). The value of \(2(Z/r(s))^{1/2}\) is adopted as the corrected plot for Hg.

Subsequently, we obtain Fig.2 by examining the relation between band gap of some elemental substance and \((Z/r(s))^{1/2}\). From fig.2, we can easily understand that the threshold of metal-semiconductor boundary is given by the \((Z/r(s))^{1/2} = 2.098\) and thus superconductivity generates in the sp-bonded elemental substances around the threshold value irrespective of whether metal or semiconductor. The threshold for sp-bonded elements may be connected with the phenomenon that the overlapping of s-band and p-band in metallic elements is resolved and new gap is just about to form.
between these bands, though not simply explained in the complex band structures. The lower limit of superconductivity in \((Z/r(s))^{1/2}\) scale may be related to the electron density though details remain unclear. Several transition metals with a value of \((Z/r(s))^{1/2}\) larger than the threshold for sp-bonded elements show superconductivity. Detailed reason is unclear but similar electronic state in Fermi surface to that in semi-conducting sp-bonded elements seems to be formed by the existence of d-band. Higher limit for transition metals depends on the both \((Z/r(s))^{1/2}\) and difference between \(r(s)\) and \(r(d)\) electrons, that is \(|r(s) - r(d)|\), and the higher limit is tentatively shown by a curve in Fig.1. At present, there is no method except to empirically determine the functional form of the higher limit by experimental data on the compounds with the contribution of d electron. Difference between \(r(s)\) and \(r(p)\), that is \(|r(s) - r(p)|(=\Delta r(sp))\), are often used as an important coordinate in the structural mapping[11,12]. The physical meaning of \(\Delta r(sp)\) has been not clearly explained but it has been suggested that \(\Delta r(sp)\) is related to sp hybridization or orbital nonlocality as indicated in the structural map of AB compounds[10,18]. Likewise, the physical meaning of \(|r(s) - r(d)|\) may be connected with sd hybridization or orbital nonlocality between s and d electrons.

When the straight line with \((Z/r(s))^{1/2}\approx1.3\) is the lower side boundary for superconductors, Mg and Sc are plotted in the domain of superconductive elements though superconductivity have not been reported in these elements. In these elements and compounds including these elements, however, superconductivity can be probably generated because some compounds such as MgB\(_2\) show superconductivity. Further, contamination, especially of oxygen, should be considered in the active elemental substances such as Sc and Y.

Examining the dependence of \(T_c\) against \((Z/r(s))^{1/2}\), Fig.3 is obtained. Excluding three elemental substances(La, Hg and Tc), the elemental substances are divided into two groups. In the one group (Group 1), the \(T_c\) value depends on \((Z/r(s))^{1/2}\) and shows the maximum for the elemental substances (such as Nb and Pb) with a \((Z/r(s))^{1/2}\) value \((\approx2.0)\) close to the threshold value\((\approx2.098)\) for metal-semiconductor boundary. In other group (Group 2), clear dependence is not shown against \((Z/r(s))^{1/2}\) value and many early transition metals belong to this group. The plots of La and Tc are fairly well placed close to the curve for Group 1 if p-character is predominant. The plot of Hg is well placed by assuming the formation of dimer.

An interesting result is obtained as shown in Fig.4 when the dependence of \(T_c/N(e)\) (\(N(e)\); number of valence electron) against \(r(s)^2\) is examined. Superconducting elemental substances are distinguished into three groups and two groups are linearly plotted, respectively, except for several transition metals belonged to third group. The value of \(N(e)\) is easily determined in the sp-bonded elements but the values are not determined in the transition metals. Here, data for transition metals are plotted in Fig.4 by giving \(N(e)=2\) tentatively. It is found in Fig.4 that three transition metals (Nb, Tc and V) are well placed in the linear relation obtained from sp-bonded elements. The findings suggest that electronic character related to superconductivity of these transition metals is similar to that of sp-bonded elements. That is, superconductivity for these elements is generated by outermost sp electrons and is approximately controlled by s electrons. Because the interatomic distances of sp-bonded elements are linearly correlated with \(r(s)\) (more precisely with the weighted average of \(r(s)\) and \(r(p))\)[19], it is interpreted that the physical meaning of \(r(s)^2\) is approximately the spatial volume occupied by s electrons. On the other hand, La, Ta, Tl and Cd are placed in other straight line but the plots of these elements can be placed close to the linear relation obtained from sp-bonded elements when the \(N(e)\) value is taken as \(N(e)=1\). According to the result by Nieminen and Hodge[20], it has been reported that the sum of s and p electron (or sp electrons) numbers is between 1.0 and 2.0 though the sum has not been calculated for all transition metals. In this study, tentative adoption of \(N(e)=2\) as the number of valence electron for transition metals may be reasonable as far as s electron is mainly the outermost one in Fermi surface though the tentative adoption is arguable. There is no clear evidence on reduction of \(N(e)\) value to 1 for La, Ta, Tl and Cd. High stability of (6s)\(^{3}\) by relativistic effect, especially in 5d transition metals, may be connected with reduction of the effective number of valence electron as the stable formation of monovalent state is indicated in Tl[21]. Conclusively, it is
suggested that the effective number of electrons related to superconductivity is probably different in between Group 1 and Group 2. The elements belonged to Group 3 show no dependence against \( r(s)^3 \) probably by two reasons; (1) the strong contribution of d electron, (2) small number of electrons related to superconductivity. Reason (1) is closely connected with bond character and the electronic state can be changed with changing cohesion state, for example from bulk to film. Taking Mo and W as the examples, the plots of Mo(film) and W(film) are placed in the straight lines of Group 1 and Group 2, respectively, because the \( T_{c,s} \) of Mo(film) and W(film) are 8K and 4.1K, respectively. Thus, the electronic state related to superconductivity can be changed by cohesion state. Further, the influence of impurity has been suggested in the superconductivity of film[22].

In near future, we will reported the two dimensional map on both superconductive elements and some compounds by similar coordinates based on \( (Z/r(s))^{1/2} \). Further, it should be noted that \( (Z/r(s))^{1/2} \) and \( r(s) \) are not best parameter for understanding of superconductivity because superconductivity is not always controlled by the electronic state of s electron alone. In further investigation, detailed understanding of superconductivity in both elemental substances and compounds will be reported by constructing modified parameters including pseudopotential radius of p electron.

![Figure 4](image)

Figure 4. Dependence of \( T_c/N(e) \) on the cube of \( r(s) \). \( N(e) \) is the number of valence electrons and it is assumed to be tentatively \( N(e)=2 \) for all transition metals.

**4. Summary**

It was tried to construct a two dimensional map based on the pseudopotential radii and its derived parameter, \( (Z/r(s))^{1/2} \), where \( r(s) \) and \( Z \) are the pseudopotential radius of s electron and valence, in order to understand the superconductivity of elemental substances. It is found that superconducting elements are well mapped by selecting the difference between pseudopotential radii and \( (Z/r(s))^{1/2} \) as the coordinates. Superconductivity in sp-bonded elements appears between \( (Z/r(s))^{1/2} \approx 1.3 \) and \( (Z/r(s))^{1/2} \approx 2.3 \). Several transition metals with a value of \( (Z/r(s))^{1/2} \) larger than the higher threshold for sp-bonded elements show superconductivity. It is indicated that the metal-semiconductor boundary for sp-bonded elements appears around \( (Z/r(s))^{1/2} \approx 2.0 \). With approaching to the boundary, further, superconducting element tends to show a higher \( T_c \) value even in the transition metals except several elements. Two linear relations between \( T_c \) and the cube of \( r(s) \) are obtained, except several transition metals, under the assumption that superconductivity attributes to s and p electrons in sp-bonded
elements and to two $s$ electrons in transition metals, though the contribution due to $d$ electrons should be considered in the exceptional transition metals.

**Acknowledgements:**

The authors thank the Yukawa Institute for Theoretical Physics at Kyoto University. Discussions during the YITP workshop YITP-W-10-12 on “International and Interdisciplinary Workshop on Novel Phenomena in Integrated Complex Sciences: from Non-living to Living Systems” were useful to complete this work. This workshop was supported in part by the Grant-in-Aid for the Global COE Program "The Next Generation of Physics, Spun from Universality and Emergence" from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan.

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