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Empirical understanding of superconducting critical temperature based on valence electron parameters

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ABSTRACT

It is tried to empirically understand the superconducting critical temperature T_c of various materials (24 elements, 286 A_nB (n = 1, 2, 3) compounds, 34 Fe- and 49 Cu-based compounds) by the effective pseudopotential radius, $r(eff)$, and the effective orbital electronegativity, $\chi(eff)(=[N(v)/r(eff)]^{1/2})$. By giving the sets of values of $r(eff)$ and the number of effective electron, $N(v)$, for 65 elements under the assumption that both the hybridization state and $N(v)$ can be assigned to 65 elements in advance by considering their electronic characters, the T_c/N(atom)–$\chi(eff)$ and T_c–$N(v)r(eff)^3$ relations are examined, where N(atom) is the number of atom in compounds. It is found that a convex triangle-like relation is obtained between T_c/N(atom) and $\chi(eff)$ and the maximum of T_c/N(atom) is observed at around the threshold $\chi(eff)$ corresponding to metal–semiconductor transition. The cuprates and Fe-compounds with the $\chi(eff)$ closer to the threshold value show the higher T_c value. Applying the linear relation between T_c and $N(v)r(eff)^3$ empirically obtained for the elements to the compounds, it is indicated that about two-thirds of A_nB compounds as well as the Fe- and Cu-based compounds are well placed along the linear relation. These results allow us to estimate the T_c value in compound materials empirically based on the effective pseudopotential radius determined by the assumed hybridization.

1. Introduction

Since Cu-based high T_c superconductor has been discovered in the last century [1], the search of new superconductors have been continued up to the present time [2–4]. The discovery of Fe-based pnictides [5] increases further interests on the search of new superconductors [6,7]. At the beginning time of the discovery of superconducting materials such as elemental metals and intermetallic compounds [8,9], the superconductivity was well explained by BCS [10] and its related theories [11]. However, the superconductivity in cuprates and Fe-based pnictides has not been explained well by BCS theory and several interpretations based on RVB mechanism [12], Fermi-liquid model [13] and spin fluctuation [14] have been proposed so far.

Though these interpretations are important for the search of new superconductors, simple methods based on some physical and/or chemical parameters are also available for practical designing and synthesis of new superconductors. Simple approaches on the search of superconducting materials have been made by the concept of the electronegativity [15] after the discovery of high T_c cuprates and several simple relations between electronegativity and T_c have been reported [16–18]. However, only insufficient results were obtained in the previous results though electronegativity is an important parameter for understanding the superconducting critical temperature (T_c). On the other hand, a successful result based on the ionic model has been reported and it has indicated that the critical temperature in cuprates can be explained by the difference in Madelung site potential of oxygen [19].

In our previous results, we have reported the possibility of understanding T_c [20,21] on the basis of pseudopotential radii and constructed the two-dimensional maps for elements and A_nB (n = 1, 2, 3) compounds by using the structural coordinates [22], which are derived from pseudopotential radii. As reported in these papers, pseudopotential radii can be connected with the orbital electronegativities of valence electrons because these radii can be defined from ℓ-dependent crossing point of the pseudopotential for respective valence electron against radial axis. Therefore, the orbital electronegativity for an arbitrarily hybridized state can be defined by averaging the constituent states in the hybridized state. Further, it is suggested in our previous papers [21,22] that the critical temperature in superconducting elements shows a convex triangle-like dependence on the average orbital electronegativity $\chi(s^np^m)$ ($1 \leqq n \leqq 2$, $0 \leqq m \leqq 6$) of s and p valence electrons. Thus, pseudopotential radius and orbital electronegativity are one of

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the promising valence electron parameters for understanding the superconducting critical temperature, respectively. In the present paper, we try to understand the superconductivity of various compounds including cuprates and Fe-based compounds by the effective pseudopotential radius and orbital electronegativity, and to examine the dependence of the critical temperature on an empirical parameter based on the pseudopotential radius.

2. Selection of valence electron parameters

In the present study, we select the valence electron parameters based on the pseudopotential radii determined by Zunger [23]. These are the effective orbital electronegativity, $\chi(eff)$, and the power functional parameter of the effective pseudopotential radius, $N(v)r(eff)^3$, where $N(v)$ is the effective electron number. The parameter is empirically selected based on our previous result [21], in which T_c is proportional to $r(s)^3$ in many elements, where $r(s)$ is the pseudopotential radius of s-electron. The effective orbital electronegativity is defined by the following equation;

$$\chi(eff) = (N(v)/r(eff))^{1/2} \quad (1)$$

The definition of $\chi(eff)$ by $N(v)$ and $r(eff)$ is based on the result by Zhang and Cohen [24]. According to their results, the Pauling's electronegativity can be given by $(Z/r(s))^{1/2}$, where Z and $r(s)$ are the valence and the Zunger's pseudopotential radius of s-electron, respectively. In the present study, it is assumed that the orbital electronegativities of p- and d-electrons can be defined in the same way by extending the equation of $\chi(s) = (Z/r(s))^{1/2}$ and, in general, the effective orbital electronegativity of valence electrons characterized by $N(v)$ and $r(eff)$ can be expressed by Eq. (1). Further, it is assumed that the value of $r(eff)$ for an arbitrary hybridized state can be given by the following equation;

$$r(s^n p^m d^k) = \frac{nr(s) + mr(p) + kr(d)}{n + m + k}, \quad (2)$$

where $r(s)$, $r(p)$ and $r(d)$ are the pseudopotential radii of s-, p- and d-electrons, respectively. The values of the pseudopotential radii determined by Zunger are used in the present study [23]. Further, n, m and k are the number of s-, p- and d-electrons, respectively.

Subsequently, it is assumed that the $r(eff)$ values of respective elements can be given by considering the hybridizing characters of valence electrons. The hybridization states are assumed in advance as follows in order to calculate the numerical values of $r(eff)$ for the respective elements.

(1) The $s^n p^m$ and $s^1 d^k$ hybridization states are assigned to the sp-bonded elements without inner d-electrons and 4d- and 5d-transition elements. For 3d-transition elements, the $s^{1.5} d^k$ hybridization state is assigned by considering somewhat high s-character. Dual characters are assumed in the post-transition elements. In the compounds of sp-elements with inner d-electrons, the hybridization states of $s^1 d^{10}$ and $s^2 d^{10}$ are assigned for Ag and Au and for Zn, Cd and Hg, respectively, while the s^1 and s^2 hybridization states are assigned to the post-transition elements in the compounds including sp-elements without inner d-electrons, respectively (see Table 1b).
(2) In the sp-bonded elements with inner d-electrons, which belong to 4th, 5th and 6th periods, the effect of the inner d-electrons is considered. In the present study, the effect is considered only in the compounds of these sp-bonded elements. In the case of these elemental substances, the $s^n p^m$ hybridization state is assigned likewise the sp-bonded elements without inner d-electrons, while, in the case of compounds of these sp-bonded elements, the $(s^n p^m + s^n p^m d^{10})/2$ and $s^n p^m d^{10}$ hybridization states are assigned to the 4th sp-bonded elements and to 5th and 6th sp-bonded elements, respectively.
(3) Further, the $sp^2 d^2$ hybridization is assumed for five special elements (V, Nb, Tc, Cu and Fe).

These values of $r(eff)$ for 65 elements are given in Table 1, together with the hybridization state and the value of $N(v)$. The $s^n p^m$ hybridization state in the sp-bonded elements (thereafter write sp-element) is easily expected from the electronic configuration of these elements but the hybridization state for transition element (thereafter write TM-element) is not simply expressed by the $s^n d^k$ hybridization because the number of s-electron delicately changes in TM-element. According to the results by Nieminen and Hodges [25], the occupation numbers of sp-electrons in transition metals

Table 1a
Effective pseudopotential radii of sp-bonded (non-transition) elements calculated from Zunger's pseudopotential radii by assuming the configurations of valence electrons in advance. Italic figures are the values of effective pseudopotential radii related to this study. E.C. means the electronic configuration.

Element	$r(eff)$ [E.C.]	$N(v)$	Element	$r(eff)$ [E.C.]	$N(v)$
Li	*0.985* [s^1]	*1*	Na	*1.10* [s^1]	*1*
Be	*0.64* [s^2]	*2*	Mg	*0.90* [s^2]	*2*
B	*0.425* [s^2p]	*3*	Al	*0.815* [s^2p]	*3*
C	*0.320* [s^2p^2]	*4*	Si	*0.710* [s^2p^2]	*4*
N	*0.258* [s^2p^3]	*5*	P	*0.624* [s^2p^3]	*5*
O	*0.215* [s^2p^4]	*6*	S	*0.553* [s^2p^4]	*6*
F	*0.182* [s^2p^5]	*7*	Cl	*0.507* [s^2p^5]	*7*

Element	$r(eff)$ [E.C.]	$N(v)$	Element	$r(eff)$ [E.C.]	$N(v)$	Element	$r(eff)$ [E.C.]	$N(v)$
K	*1.54* [s^1]	*1*	Rb	*1.67* [s^1]	*1*	Cs	*1.71* [s^1]	*1*
	0.955 [$s^{0.5}d^{0.5}$]	*1*		*1.190* [$s^{0.5}d^{0.5}$]	*1*		- [$s^{0.5}d^{0.5}$]	*1*
Ca	*1.32* [s^2]	*2*	Sr	*1.42* [s^2]	*2*	Ba	*1.515* [s^2]	*2*
	0.830 [s^1d^1]	*2*		*1.027* [s^1d^1]	*2*		*1.228* [s^1d^1]	*2*
Ga	*0.818* [s^2p]	*3*	In	*0.997* [s^2p]	*3*	Tl	*1.083* [s^2p]	*3*
	0.569 [$(s^2p + s^2pd^{10})/2$]	*3*		*0.507* [s^2pd^{10}]	*3*		*0.606* [s^2pd^{10}]	*3*
Ge	*0.780* [s^2p^2]	*4*	Sn	*0.940* [s^2p^2]	*4*	Pb	*1.045* [s^2p^2]	*4*
	0.559 [$(s^2p^2 + s^2p^2d^{10})/2$]	*4*		*0.515* [$s^2p^2d^{10}$]	*4*		*0.620* [$s^2p^2d^{10}$]	*4*
As	*0.715* [s^2p^3]	*5*	Sb	*0.893* [s^2p^3]	*5*	Bi	*1.014* [s^2p^3]	*5*
	0.528 [$(s^2p^3 + s^2p^3d^{10})/2$]	*5*		*0.521* [$s^2p^3d^{10}$]	*5*		*0.630* [$s^2p^3d^{10}$]	*5*
Se	*0.652* [s^2p^4]	*6*	Te	*0.850* [s^2p^4]	*6*	Po	0.973 [s^2p^4]	*6*
	0.495 [$(s^2p^4 + s^2p^4d^{10})/2$]	*6*		*0.522* [$s^2p^4d^{10}$]	*6*		0.631 [$s^2p^4d^{10}$]	*6*
Br	0.609 [s^2p^5]	*7*	I	0.809 [s^2p^5]	*7*	At	0.943 [s^2p^5]	*7*
	0.472 [$(s^2p^5 + s^2p^5d^{10})/2$]	*7*		0.469 [$s^2p^5d^{10}$]	*7*		0.668 [$s^2p^5d^{10}$]	*7*