学 位 論 文 の 要 約

題目　Chemical Interpretation of Superconductivity by Valence Electron Parameters

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序論

It has been tried to interpret the generation of superconductivity in various materials and their critical temperatures (T_c) by the valence electron parameters based on the pseudopotential radii (*r(s)*, *r(p)* and *r(d)*) for 65 elements, where *r(s)*, *r(p)* and *r(d)* are the pseudopotential radii of s, p and d-electrons, respectively. Selecting the effective orbital electronegativity ($\chi(eff)=(N(v)/r(eff))^{1/2}$) and the effective electron number ($N(v)$) as the valence electron parameters, which are given in advance by assuming the hybridization states for 65 elements, the two-dimensional maps for various compounds have been constructed and the relations of $T_c/N(atom\text{-}\chi(eff)$ and $T_c\text{-}N(v)r(eff)^3$ have been examined for the various compounds including high-T_c superconductors. It has been indicated that $\chi(eff)$ and the parameter $N(v)r(eff)^3$ are the effective measures for the empirical search of a new superconductor.

Chapter 1　Introduction

The historical background and the purpose of the present thesis are explained. The importance of the physical parameters is stressed by exemplifying the construction of the crystal structure maps and syntheses of the pseudobinary nitrides in the previous papers. The purposes of the thesis are the understanding of the superconducting materials systematically by constructing the two-dimensional maps of various superconducting compounds and the perspective interpretation of superconducting critical temperature based on the pseudopotential radius and the concept of hybridization.

Chapter 2　Pseudopotential radius and orbital electronegativity

The reasons for selecting pseudopotential radius and orbital electronegativity as the two valence electron parameters and their meanings are explained from physical and chemical standpoints. Further, the possibility of applying these parameters to superconductivity is discussed.

Chapter 3 Superconductivity in elements and interpretation of critical temperature(T_c) by valence electron parameters

It has been tried to interpret the superconductivity and its critical temperature(T_c) in the elemental substances by the orbital electronegativity of the s electron, $(Z/r(s))^{1/2}$, which is defined by the pseudopotential radius of the s electron, $r(s)$, and the valence, Z. Dependence of critical temperature(T_c) on $(Z/r(s))^{1/2}$ shows a concave curve with a maximum around $(Z/r(s))^{1/2}=2.0$, except for several substances and it is found that the elemental substances with higher T_c such as Nb and Pb have a $(Z/r(s))^{1/2}$ value close to the threshold one corresponding to the change from metal to semiconductor. Many exceptional substances can be plotted close to the concave curve by considering the effect of the p electron or by changing the cohesion state from bulk to film, suggesting the increase of T_c value due to the increase of s- and/or p-characters, though the critical temperature for metastable elemental substances is not completely explained by the orbital electronegativity of the s electron.

Chapter 4 Two-dimensional mapping of superconducting materials based on pseudopotential radii

Two dimensional diagrams for superconducting elements and A_nB(n=1, 2, 3) compounds have been constructed by using the difference (Δr_{ENav}) between Zunger's pseudopotential radii and the orbital electronegativity($[(Z/r(s^n p^m))^{1/2}]_{ENav}$) derived from the pseudopotential radii. It is found that both superconducting elements and A_nB compounds are well placed in the same domain surrounded by four boundary lines in the Δr_{ENav}- $[(Z/r(s^n p^m))^{1/2}]_{ENav}$ diagram. For sp-bonded elements, the boundary for superconducting/non-superconducting(SC/non-SC) is determined by a constant orbital electronegativity of $[(Z/r(s^n p^m))^{1/2}]_{ENav} \cong 2.3$, which is close to the boundary ($[(Z/r(s^n p^m))^{1/2}]_{ENav} = 2.046$) for the metal-semiconductor transition. Superconducting elements and compounds with relatively high T_c values have an orbital electronegativity

close to the value ranging between SC/non-SC and metal-semiconductor transition boundaries. It is suggested that arithmetically averaging of electronegativity is inadequate in AB-type transition metal nitrides and carbides.

Chapter 5 Dependence of superconducting critical temperature on the pseudopotential radii

Relation between the critical temperature and the pseudopotential radii has been examined in the superconducting elements, AB-type compounds, Fe- and Cu-based compounds by using the effective pseudooptential radii(*r(eff)*) assumed from the pseudopotential radii of s-, p- and d-electrons in advance. It has been indicated that the critical temperature(T_c) for many superconducting materials can be estimated by the functional form, $N(v)r(eff)^3$, of the effective number of valence electron(*N(v)*) and the effective pseudopotential radius. The value of T_c shows a highly linear relation to $N(v)r(eff)^3$ by assuming the p^3d^n or sp^2d^n hybridization for the elements connected with relatively high T_c such as V, Nb and Tc in elements and AB compounds, Cu in cuprates and Fe in pnictides and chalcogenides. The findings suggest that the p^3d^n or sp^2d^n hybridization is a key bonding character for generating high T_c in various superconducting materials.

Chapter 6 Relations between the critical temperature and the valence electron parameters

It has been 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 in advance under the assumption that both the respective hybridization state and *N(v)* can be assigned to 65 elements by considering their chemical characters, both 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 between $T_c/N(atom)$ and $\chi(eff)$ is obtained for the elements, A_nB(n=1, 2, 3) compounds and both Fe- and Cu-based

superconductors, in which the maximum of $T_c/N(atom)$ is placed at around the value of $\chi(eff)=2.046$ corresponding to the threshold of metal-semiconductor (M-S) transition. It is indicated that the cuprates and Fe-compounds with the orbital electronegativity closer to the threshold $\chi(eff)$ value show the higher T_c value, respectively.

Examining the T_c-$N((v)r(eff)^3$ relation for the elements by using the sets of values of $r(eff)$ and $N(v)$, a linear relation (given by $T_c=1.70N((v)r(eff)^3-0.70$) is obtained empirically. About two-thirds of A_nB compounds as well as the Fe- and Cu-based compounds are well placed along the linear relation obtained from the elements. These results allow us to estimate the T_c value in compounds empirically based on the effective pseudopotential radius determined by the assumed hybridization.

Chapter 7 Summary of the thesis

It has been indicated that the critical temperature (T_c) can be empirically estimated by the valence electron parameters of $\chi(eff)$ and $N((v)r(eff)^3$ based on pseudopotential radius. The availability of the empirical relations of both the $T_c/N(atom)$-$\chi(eff)$ and T_c-$N((v)r(eff)^3$ are expecting for the search of new superconductors.