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Structural classification and a binary structure model for superconductors*

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Based on structural and bonding features, a new classification scheme of superconductors is proposed to classify them into three classes: three-dimensional, two-dimensional and molecule-assembled superconductors. The 'sandwich model' for the high-T_c cuprates is extended to a 'binary structure model': i.e., the crystal structure of most superconductors can be partitioned into two parts, a superconducting active component and a supplementary component. Partially metallic covalent bonding is found to be a common feature in all superconducting active components, and the electron states of the atoms in the active components usually make a dominant contribution to the energy band near the Fermi surface. Possible directions to explore new superconductors are discussed based on the structural classification and the binary structure model.

Keywords: superconductors, crystal structure, chemical bond, model
PACC: 6150L, 7470, 7410, 7400

1. Introduction

Since the discovery of high-T_c superconductivity in 1986,[1] progress has been made unceasingly in the exploration of high-T_c materials and the investigations of superconducting mechanism. Many important cuprate systems (for example, the La, Y, Bi, Tl and Hg based systems) have been studied extensively[2] and their structural classifications have been proposed by a number of authors.[3–6] Although there is no common consensus about the mechanism for high-T_c superconductivity so far, many high-T_c cuprates have been obtained based on empirical relations between their structure and superconductivity.[2] Recently, a number of new non-cuprate superconductors have been found, such as KOs_2O_6,[7] $Na_{0.35}CoO_2{\cdot}1.3H_2O$,[8] MgB_2[9] and so on. The family of superconductors has rapidly expanded and abundant information about thousands of superconductors is now available. Therefore, we believe that careful inspection of the existing superconductors can not only provide us with clues to explore new materials but also shed light on the mechanism of superconductivity.

Proper classification of structures and examinations of the bonding nature of the existing superconductors are of crucial importance for the rational design and crystal engineering of new superconductors. According to the physical and chemical properties, superconductors are often classified into various classes such as type I and type II, high T_c and low T_c, organic and inorganic, and so on. However, these classifications cannot provide explicit information about the structural feature of the materials.

In this paper we emphasize the crucial importance of covalent bonding in superconductors, which has been noticed by many authors. In 1974, Goodenough proposed a conceptual T–b phase diagram in which a superconducting state is stabilized for large b (greater than a critical value b_{cs}) at low temperatures, where b is the transfer energy that measures the strength of interaction between localized orbitals. In a solid with significant cation–cation interactions, b can be related to R^{-1}, where R is the cation–cation separation. When cation–anion–cation interaction is important, b is approximately proportional to λ^2, where λ is the covalent mixing parameter.[10] It is clear that superconductivity may occur in systems with high covalency. In 1978, Cowan and Carbotte examined the effect of mixing of the localized state (e.g. covalent bond) with conduction electrons and found that a sizeable enhancement of superconducting T_c can occur.[11]

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Soon after the discovery of the high-T_c superconductivity, Urland pointed out that the occurrence of superconductivity was associated with the cooperative action of electron delocalization, localization and correlation with comparable energy distribution.[12] More recently, Simon *et al* have proposed that the origin of superconductivity is the tendency of conduction electrons towards a pairwise localization.[13,14]

In this paper, we propose a classification scheme of the crystal structures of superconductors by inductive analysis, and classify them into three classes according to their spatial structure and bonding nature. Then, we extend the 'the sandwich model' for the cuprates[15] to a 'binary structure model' for other superconductors; namely, most superconductors are regarded as being composed of a superconducting active component and a supplementary structure component. The feasibility of the binary structure model will be discussed based on the analysis of the chemical bonding nature within the active component. Partially metallic covalent bonding is found to be a common feature in all superconducting active components. Finally, we will point out some possible directions for exploration of new superconductors according to the structural classification and the binary structure model.

2. Structural classification of superconductors

Based on the structural dimensions, most superconductors were usually divided into two classes: the three-dimensional (3D) and the quasi-two-dimensional (2D). In addition, some organic superconductors are called quasi-one-dimensional (1D) superconductors because they show very good conductivity merely along one direction. Except for a few amorphous ones, all superconductors are crystalline solid with 3D periodic structure. Therefore, the difference between the 2D superconductor and the 3D superconductor does not depend on whether they possess 3D periodicity, but depends on their bonding strength along different directions. The general structural characteristics of the 2D layered superconductors are that they have stronger intra-layer bonds and weaker interlayer bonds. In the same way, we may define the superconductors with strong intramolecular bonding and weak intermolecular bonding as the molecule-assembled structure type. Thus, according to their spatial characteristics of the chemical bonding, the crystal structures of superconductors can be classified into three classes: the 3D structure, the 2D layered structure and the molecule-assembled structure. In the molecule-assembled structure, 'molecule' is here a generalized concept that includes real organic molecules, atom clusters and atomic cages. Typical examples of the three structural classes of superconductors will be presented and discussed in the following.

2.1. Superconductors with 3D structure

The structural characteristics of 3D superconductors are that the atoms have identical (or almost the same) bond lengths and bonding strengths extended in the 3D space. The chemical bonds forming the 3D skeleton are mainly covalent. The majority of the 3D superconductors have high symmetry. They usually belong to cubic or hexagonal crystal systems.

All superconducting metal elements belong to the 3D structure class, including the body-centred cubic (BCC), the face-centred cubic (FCC) and the hexagonal close packing (HCP) structures. Some metals, such as Hg, In, Ga and Sn with distorted close-packing structure, may also be classified into this class. Moreover, many oxides and intermetallic compounds with cubic symmetry belong to this class. Table 1 listed some typical examples of the 3D superconductors. The $Ba_{0.6}K_{0.4}BiO_3$with perovskite structure has the highest T_c in this class at present.

It should be mentioned that only representative examples of the 3D structure superconductors are listed in Table 1, so the list is far from complete. The same is true for the 2D structure and the molecule-assembled superconductors listed in Table 2 and Table 3.

2.2. Superconductors with 2D layered structure

The structural characteristics of the 2D layered superconductors are that the atoms have identical (or almost the same) bond lengths and bonding strengths in two-dimensional space, and the interatomic bonds within the layers are mainly covalent bonds. Typical 2D layered superconductors are the intercalated graphite and bisulfides. This class of superconductors also covers many important systems such as the layered cuprates, MgB_2, Na_xCoO_2 yH2O, *RE*-*M*-B-C (*RE* = rare earth, *M*=Ni, Pd), Li intercalated β-ZrNCl and so on. Table 2 shows typical superconductors that belong to the 2D layered structure class.

Table 1. Typical superconductors belong to the 3D structure class.

Structure type	typical 3D superconductors and T_c (K)
A2 (W type, BCC)	V (5.4), Nb (9.25)
A1 (Cu type FCC)	Al (1.17), Pb (7.2),
A3 (Mg type, HCP)	Re (1.7), La (6), Tc (8.2)
Distorted close packing	In (3.4), Sn (3.7), Hg (4.15), Ga (7.9)
A15 (Cr_3Si)	V_3Si (17.1), Nb_3Sn (18.1), Nb_3Ge (23.2)
C15 ($MgCu_2$)	$ZrZn_2$(0.6), $CeRu_2$ (6.5), ZrV_2(8.8)
B1(NaCl)	NbC (11), MoC (14.3), NbN (18.0)
Perovskite	$BaPb_{0.75}Bi_{0.25}O_3$(13), $Ba_{0.6}K_{0.4}BiO_3$(30)
Antiperovskite	$MgCNi_3$ (8.0)
Spinel	$CuRh_2Se_4$ (3.48), $CuRh_2S_4$ (4.70), $LiTi_2O_4$ (13)
Pyrochlore	$Cd_2Re_2O_7$ (1.47)
β-pyrochlore	$RbOs_2O_6$ (6.3), KOs_2O_6 (9.6)
Tungsten bronzes	$K_{0.18}WO_3$(4), $Cs_{0.2}WO_3$(6.7), $Rb_{0.26}WO_3$(7)

Table 2. Typical superconductors belonging to the 2D layered structure class.

Structure type	typical superconductor and T_c (K)
K_2NiF_4	Sr_2RuO_4(1), $La_{1.84}Sr_{0.16}CuO_4$ (38.5)
Nd_2CuO_4	$Nd_{1.85}Ce_{0.15}CuO_4$(24)
RE-123	$YBa_2Cu_3O_7$(92)
AlB_2	ZrB_2(5.5), $NbB_{2.34}$(9.8), MgB_2(39)
$Na_xCoO_2{\cdot}yH_2O$	$Na_{0.35}CoO_2{\cdot}1.3H_2O$ (5)
YNi_2B_2C	$LuNi_2B_2C$ (16.5), YPd_2B_2C (23.1)
β-ZrNCl	β-ZrNCl (13), $Li_{0.48}(THF)_yHfNCl$ (25.5)
Intercalated graphite	NaC_2 (5), YbC_6(6.5), CaC_6 (11.5)
Intercalated bisulfide	$K_{0.4}MoS_2$ (6.9), $CsTaS_2$(8.1)
$ThCr_2Si_2$	URu_2Si_2(0.8)

There is no clear-cut border between the 3D and the 2D structures. Some superconductors can be considered as the intermediate type between the 3D and 2D classes because the interlayer bonding strength is comparable to the intra-layer bonding strength within their crystal structures. For example, the Cu–O bond length with the apical oxygen is only slightly longer than that within the CuO_2 plane in the Y-123 structure, so the interlayer bonding is comparable to the intra-layer bonding. $RENi_2B_2C$ (RE = rare earth) is another intermediate type of superconductor where the direct B–C covalent bond is formed between the NiB layers and the REC layers. MgB_2 is also an intermediate type of superconductor because there is quite strong ionic bonding between Mg^{2+} and B^- sheets with a graphite-like structure. It should be mentioned that all these superconductors of the intermediate type have relatively high T_c. It can be inferred that the higher T_c could be obtained by properly adjusting the interlayer bonding strength for a specific 2D superconductor.

In the known superconductors with 2D layered structure, the cuprates have the highest T_c while MgB_2 has the highest T_c among others.

2.3. Superconductors with the molecule-assembled structure

The molecule-assembled superconductors contain organic molecules, atom clusters or cages as the major components in the structure, and the remaining part are usually atoms or ions located between the molecules or inside the cages. The intramolecular bonds are much shorter and stronger than the intermolecular bonds. The chemical bonds within the molecules are dominantly covalent. This class con-

tains not only organic superconductors and the doped C_{60} but also the clatherate and the Chevrel phase superconductors. Intermetallic compound YRh_4B_4 also belongs to this class (Table 3). In the known superconductors with molecule-assembled structures, the alkali metal doped C_{60} ($RbCs_2C_{60}$) have the highest T_c while T_c of the Chevrel phases are relatively high among others.

The classification method proposed above is based on the crystal structure characteristics of the superconductors. This method is not only helpful to understand and categorize the vast existing superconductors, but also provides us with possible routes for designing new superconductors.

Table 3. Typical superconductors belonging to the molecule-assembled structure class.

Structure type	typical superconductor and T_c(K)
TMTSF-X	$(TMTSF)_2PF_6$ (1.2), $(TMTSF)_2TaF_6$ (1.4)
$\kappa-(ET)_2X$	$\kappa-(ET)_2Cu[N(CN)_2]Cl$ (12.8)
K_3C_{60}(FCC)	Rb_3C_{60}(29), Rb_2CsC_{60}(31), $RbCs_2C_{60}$(33)
Ba_6C_{60}(BCC)	Sr_6C_{60}(4), Ba_6C_{60}(6)
Chevrel phase	$SnMo_6S_8$ (14.5), $PbMo_6S_8$ (15.2)
$Rb_{2n}(Mo_9S_{11})(Mo_{6n}S_{6n+2})$	$n = 1$ (4.2), $n = 2$ (11), $n = 3$ (7), $n = 4$ (5.8)
$CeCo_4B_4$	$ErRh_4B_4$(0.65), YRh_4B_4(11.3)

3. Binary structure model of superconductors

All the layered cuprate superconductors have crystal structures consisting of electronically active CuO_2 superconducting layers sandwiched between the charge reservoir layers.[10] This 'sandwich model' for cuprates can be extended to other superconductors. By the inductive analysis of the structural features, most crystal structures of known superconductors can be considered as built of two components, a superconducting active component (SAC) and a supplementary structure component (SSC). The SAC and SSC act like the CuO_2 layers and the charge reservoir layers in the cuprates respectively. The conductivity and superconductivity occur within SAC, and SSC acts to stabilize the structure, to realize the charge balance and to adjust the carrier density and energy state density. This extended sandwich model is called a 'binary structure model' of superconductors for brevity. In the following, we will show how to partition most structures of superconductors into two parts (SAC and SSC) according to their structural and bonding features. In the process of chemical topology study of ternary and quaternary superconductors, King proposed a method to partition the structures into two parts: the positive ions of the alkali, alkaline earth, lanthanide, or actinide metal, and the negative-charged anionic networks formed by the remaining elements. The nature of the anion sub-networks determines the electrical properties of the compounds.[16] Our method is similar to that used by King, but the SAC can be a covalent-bonding cation as well. SAC and SSC for some representative superconductors are listed in Table 4.

The binary structure model proposed here is based on the crystal structure data of superconductors as well as the theoretical results of their electronic structure calculation. Just as the physical and chemical properties of an organic molecule is mainly determined by its 'frontal orbital': the highest occupied molecule orbital (HOMO) and lowest unoccupied molecule orbital (LUMO), the physical properties of a solid are mainly determined by its energy bands with relatively high energy, such as the conduction and valence bands in a semiconductor or the band structure nearby the Fermi surface in a metal.[17] Because SSC are usually stable ions (see Table 4.) with electron energy far below the Fermi energy, the electron states of the atoms in the SAC usually make a dominant contribution to the energy band near the Fermi surface. This is the theoretical foundation for the binary structure model because the electrical properties of materials mainly depend on the electronic structure near the Fermi surface, which is dominated by the electron states of the atoms in the SAC. For example, the CuO_2 layers are the common building block in cuprate superconductors, and the results of the electronic structure calculation indicate that the electron states of the Cu 3d and O 2p make a dominant contri-

bution to the energy band near the Fermi surface.[18] The electronic structure near the Fermi surface plays a dominant role in the electrical properties including superconductivity. Therefore, the CuO_2 layers are the SAC in cuprate superconductors.

Table 4. SAC and SSC for some representative superconductors.

Typical superconductor	SAC	SSC
Nb_3Ge	Nb (or V) chains	Al, Si, Ge, Sn
ZrV_2	V sublattice	Zr, Hf
$Ba_{0.6}K_{0.4}BiO_3$	BiO_3 sublattice	K^+, Ba^{2+}, Sr^{2+}
$MgCNi_3$	CNi_3 sublattice	Mg^{2+}
$LiTi_2O_4$	Ti_2O_4 sublattice	Li^+
$Cd_2Re_2O_7$	Re_2O_7 sublattice	Cd^{2+}
KOs_2O_6	Os_2O_6 sublattice	K^+
A_xWO_3	WO_3 sublattice	A = (Na, K, Rb, Cs)
$La_{2-x}Sr_xCuO_4$	CuO_2 layers	LaO layers
$YBa_2Cu_3O_7$	CuO_2 layers	Y, BaO
MgB_2	B layers	Mg^{2+}
$CeCu_2Si_2$	Cu_2Si_2 layers	Ce
YNi_2B_2C	Ni_2B_2 layers	YC layers
$Li_{0.48}(THF)_yHfNCl$	HfNCl layers	Li^+, Na^+
$Na_xCoO_2\ yH_2O$	CoO_2 layers	Na+, H_2O
KC_8	Graphite layers	K^+
$CsTaS_2$	TaS_2 layers	Cs^+
A_3C_{60}	C_{60}molecule	Metal ions A^+
$PbMo_6S_8$	Mo_6S_8 cluster	Pb
UBe_{13}	Be_{13} cluster	U
$(TMTSF)_2PF_6$	$(TMTSF)_2$ molecule	PF_6, AsF_6, etc
$\kappa-(BEDT\text{-}TTF)_2X$	BEDT-TTF molecule	X = Cl, Br, I
$\tau-(ET)_2I_3$	ET molecule	I

3.1. The superconducting active components

The SAC is generally a structural part connected by chemical bonds that are dominantly covalent. It may be a 3D skeleton network, a 2D atomic layer, or a molecule or an atom cluster. General characteristics of the SAC can be summarized as follows.

A. Bonding covalence: In the SAC, the atoms are connected by either non-polar or polar covalent bonds. Usually, the bond lengths are short and the bond strengths are strong in the SAC so that they are structurally stable. The SAC usually does not change in a series of superconductors.

B. Electron delocalization: Electrical conduction is the precondition for the active components. Therefore, the SAC must contain delocalized (multicentred) bonds so that certain valence electrons are delocalized. In addition to the metallic bonding in metals and alloys, the electron delocalization can be realized in other materials with resonating-valence bonds or delocalized π bonds. Using the chemical bond description, the active components need to contain partially metallic covalent bonds; from the energy band approach, the active components must have sufficient electrons (or holes) in the conduction band, which may be obtained by suitable carrier doping.

C. Atom doping sensitivity: The superconductivity is usually sensitive to the atom doping and substitution within the SAC. In most cases, such doping or substitution causes rapid decrease of T_c. For this reason, SAC should be kept as pure as possible, and substitutions in SAC are only feasible by elements with very close chemical characters such as ionic size, valence and electron configuration. In order to avoid the carrier localization in SAC, the elemental doping and substitution in SSC are preferred.

D. Chemical environment equivalence: The atoms in SAC generally have identical chemical environ-

ments, i.e. they usually occupy crystallographically equivalent sites. This is essential to the electron delocalization as electrons can move around different positions without sizeable energy change.

The SAC in a layered superconductor is generally obvious, which is typically the most stable layers in the structure, such as the boron layers in MgB_2 and the graphite layers in the graphite intercalated compounds where covalent bonding dominates. In the molecule-assembled superconductors, the active components are in most cases the molecules, the atom clusters or the atomic cages with delocalized bonds.

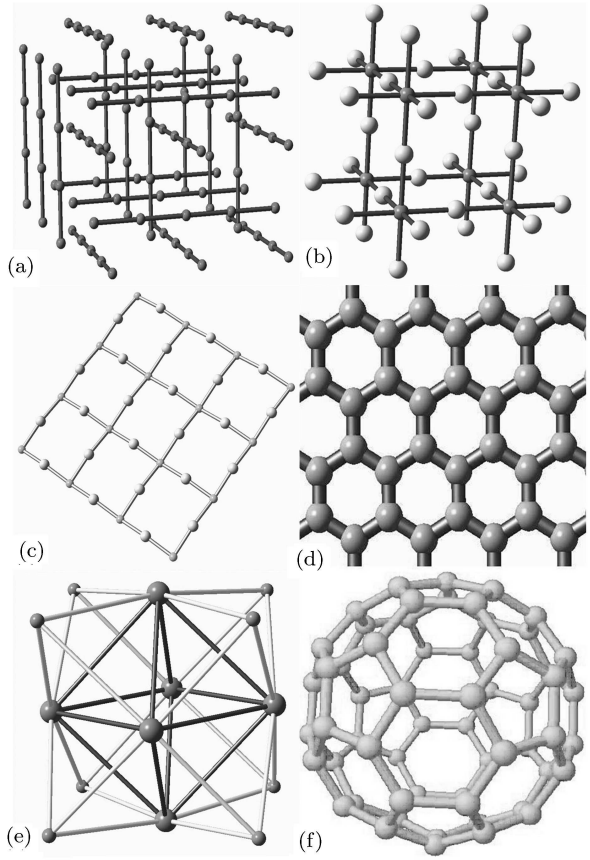


Fig.1. Representative superconducting active components. (a) Nb chains in Nb_3Ge. (b) BiO_3 sublattice in $K_{0.4}Ba_{0.6}BiO_3$. (c) CuO_2 layer in $YBa_2Cu_3O_7$. (d) Graphite-like B layer in MgB_2. (e) Mo_6S_8 cluster in $PbMo_6S_8$. (f) C_{60} molecule.

The SAC in a 3D superconductor can be determined according to the bond covalency, the nearest-neighbour atomic spacing, the doping sensitivity or the calculated electronic structures. The chemical bonds within the SAC usually show more covalent character than other bonds. If the bond lengths are different, then the active component is usually the atom groups connected by short bonds. For example, Nb_3Ge has an A15 structure where the Nb–Nb bond length is shorter than the Nb–Ge bond length, so we may regard the Nb chains as the active component. Doping sensitivity can also be used to find the SAC if the experimental results of superconductivity of doping and substitution are available. Moreover, the SAC can also be determined using the results of electronic structure calculations, because the electron states of the atoms in the SAC usually make a dominant contribution to the energy band near the Fermi surface. Several representative SACs are illustrated in Fig.1.

A superconductor may be composed of merely an active component. If all the nearest-neighbour atomic distances are equal, then the whole structure may be regarded as the SAC. For instances, superconducting metal elements and some alloys contain only SAC without SSC. Note that most of these superconductors contain elements with d or p valence electrons where the localized covalent bonds coexist with the delocalized metallic bonds.

3.2. The supplementary component

The SSC functions resembling the carrier reservoir layers in the cuprates, and it plays at least one of the following roles: (1) to stabilize the spatial structure; (2) to maintain the charge balance; (3) to adjust the carrier concentration and the energy state density.

The SSC may be a single ion, atom or normal-valence molecule, or an insulating layer or their mixtures. Chemical bonds between SSC and SAC, being either van der Waal or ionic type, are generally weaker than that within the SAC. Take the $Na_{0..35}CoO_2{\cdot}1.3H_2O$ structure as an example, where Na^+ cations and the H_2O molecules form the SSC, and the CoO_2 layers are the SAC.

The cations of the alkali, alkaline earth, lanthanide, or actinide metals and halogen anions (such as F^- and Cl^-) are quite stable in their ionic form, and the covalent contribution is rather insignificant in their bonding. Therefore, these elements usually form the SSC, acting as the electron donor or acceptor in the structure. Table 4 shows the results of the SAC and SSC partition for some representative superconductors.

The crystal-structure classification and the binary structure model for the superconductor proposed here are helpful not only for interpreting experimental observations of known superconductors, but also for exploring new superconductors as discussed below.

4. The chemical bonds in superconductors: partial-metallic covalent bonds

Since we have emphasized the importance of the coexistence of the localized covalent bonds with the delocalized (metallic) bonds in the SAC, a criterion is needed to judge the formation of the covalent bonds. Here, we use the empirical Hannay–Smyth equation[19] to estimate the percentage of ionicity based on Pauling's electronegativity:

Ionic character of the

$$A\text{-}B \text{ bond } = 0.16|\chi_A - \chi_B| + 0.035|\chi_A - \chi_B|^2 . \quad (1)$$

According to Eq.(1), we can find that the ionic character of the A–B bond is 46% when the electronegativity difference ($\Delta\chi$) is equal to 2. Explicitly, covalent bonding is dominant ($> 50\%$) when $\Delta\chi$ is less than 2. Most values of $\Delta\chi$ for the atoms in the SAC given in Table 4 are less than 1.7, so their ionic characters are less than 38%, resulting in the covalent character greater than 62%. Although the Ti–O bond of $LiTi_2O_4$ has the highest $\Delta\chi(\Delta\chi = 2.0)$ among the SACs given in Table 4, it is polar covalent. In addition, the electropositive cations can increase the covalency of the bonds between transition metals and oxygen.[20] The presence of Li^+in $LiTi_2O_4$ will further increase the covalency of the Ti–O bonds. Therefore, covalent bonding is the common feature in all SACs listed in Table 4. In the high-T_c oxides, high covalency is necessary to develop bands capable of superconducting metallic behaviour.[20] Covalent contribution can be found in intermetallic compounds when the bond length is shorter than the sum of the metal radii. In the ionic crystals, the ion polarization effect also brings about the bond-length shortening and the formation of partially covalent bonds.

Typical ionic compounds, such as KF, NaCl and BaO, are insulators, not superconductors, because the electrons are localized at the sites of cations or anions. Therefore, we can simply say that the materials with pure or nearly pure ionic bonds cannot be a superconductor. Many organic and inorganic materials with typical two-electron–two-centre (2e2c) covalent bonds, such as hydrocarbons (C_nH_{2n+2}), NB and diamond, are insulators, and they are not superconductors in their high-purity form. Thus, we can say that the materials with pure covalent (2e2c) bonds cannot be superconducting. It is rational that materials with pure ionic or covalent bonding is not superconducting, because all valence electrons are localized. A more interesting phenomenon is that the metals that can be properly described by the free-electron model, such as alkali metals with nearly perfect (spherical) Fermi surface, are not superconductors under atmospheric pressure. Most alkaline earth metals are not superconducting, and the only exception is the metal Be ($T_c = 0.026$ K) which shows the predominant covalent-bonding tendency due to its small atomic radius and relatively large electronegativity. Even the coinage metals, Cu, Ag and Au with filled d orbitals and one valence s electron ($d^{10}s^1$), are not superconductors. Most superconducting metals have d or p valence electrons.[21] The unfilled d and p orbitals, being angle-dependent, prefer to be involved in the formation of directional covalent bonds. Although the diffused p orbitals usually generate stronger covalent bond by larger overlap than the compact d electrons, the d electrons are better described by the tight-binding models than by the free-electron model. Some covalent contribution must exist in the bonding process when p or d valence electrons are involved. Therefore, we can also say that materials with pure metallic bonds cannot be a superconductor. Here, pure metallic bond means that valence electrons can be treated by the free-electron gas model.[22] Metals, which can be described properly using the free-electron gas model, must have negligible electron–phonon interactions. This is in consistence with the BCS theory where the electron–phonon interactions are necessary for the occurrence of superconductivity. Therefore, the chemical bond must be of a mixed or transitional type in a superconductor. Because many metallic elements, even some non-metal elements under high pressure, are superconductors,[21] where the ionic bonding is negligible if not completely impossible, ionic bond can be excluded as a necessary bond type in a superconductor. So, we can have the conclusion that the characteristics of chemical bonds in a superconductor is the coexistence of covalent (localized) bonds and metallic (delocalized) bonds; or the precondition for a material to be superconductor is that it contains partially-metallic covalent bonds.

Many superconductors can be regarded as a product of carrier doping in a covalent solid, either an insulator or a semiconductor. Two electrons having opposite spins in a simple covalent bond are paired locally between the bonding atoms. The carrier doping introduces 'defects', i.e. unpaired electrons or holes, in the

covalent framework, and superconductivity may occur in such a 'defective' covalent-bonding system. Except in ferromagnetic materials, electrons with opposite spins usually prefer to form pairs. Within the 'defective' covalent-bonding system, most electrons are involved in the formation of covalent bonds, and spin pairing are realized in the bonding processes between the nearest atoms; the remaining electrons, which cannot find electrons with opposite spin to form local spin pairs with the nearest atoms, may participate delocalized multi-centred bonds in resonating valence states. Firstly, the unpaired electrons are delocalized and can move fairly freely; secondly they have the tendency to form spin pairs with electrons in a longer range than in a normal covalent bond. These distant electron pairs are much weakly tied as compared with the pairs in a normal covalent bond so that they are stable only at low temperatures. Such distant electron pairs might play the role of the Cooper pairs as in the BCS theory. Excellent experimental evidence has been obtained recently by Ekimov *et al*[23] for the superconductivity in the 'defective' covalent-bonding system. They reported the discovery of superconductivity around 4K in boron-doped diamond. It is quite remarkable that diamond, a typical covalent material, can become a superconductor when heavily doped with boron at high pressure and temperature. It should be mentioned here that the doping density in a superconductor, generally near 10% or more, is much bigger than that in a commonly encountered semiconductor.

Based on the above discussions, we may draw a conclusion that the coexistence of covalent bonding and the metallic bonding is a necessary condition for the occurrence of superconductivity. In general, the basic strategy to make a superconductor is to introduce partially metallic bonds in a covalent-bond based system by carrier doping, or to introduce the covalent bonds in a metallic-bond based system by combining with nonmetal or metalloid elements.

5. About new superconductor exploration

The exploration of new superconductors is one of the greatest challenges to human wisdom. In the following, we will discuss some possible directions for the exploration of new superconductors based on our structural classification and the binary structure model.

A renowned material scientist Rustum Roy[24] once pointed out that the first step of material research is to identify critical structure element correlated with desired property. In the binary structure model, the SAC is the critical structure element for superconductivity. The exploration of new superconductors can begin with the design of the SAC.

According to the structural classification and the binary structure model, searching for new superconductors may be reduced to the finding of new SAC in 3D, 2D and molecule-assembled systems. More attention should be paid to the 2D layered or molecule-assembled systems, because they are relatively easy to be doped with electrons (or holes), and most existing superconductors with T_c above 20 K belong to these two classes. Furthermore, the interlayer and intermolecule interactions can be flexibly adjusted by altering the SSC in these systems. Particularly, structures and properties of the molecule-assembled materials (and nanotubes) may be continuously changed in a very broad range, from insulating molecules to semiconducting, conducting or even superconducting materials.

According to the first two basic characteristics of SAC, i.e. bonding covalence and electron delocalization, we must choose systems containing mixed-valence ions or atoms capable of forming delocalized π bonds (or other resonating bonds) to make a SAC. Generally, the mixed-valence ions are the transition or the post-transition metal ions. The best elements to make covalent bonds are the non-metals in the second row of the periodic table, such as B, C, N and O. Other non-metals, such as Si, P and S, are also good candidate elements to form covalent bonds. Thus, we can obtain a rough idea about the chemical composition of the superconductors. In fact, many superconductors with relatively high T_c are compounds containing these non-metal elements, such as MgB_2, $RbCs_2C_{60}$, NbN and high-T_c cuprates. At present, only oxide systems, especially the multi-component cuprates, have been studied extensively. We are now in possession of knowledge about the superconductivity of most binary borides, carbides and nitrides. However, enormous ternary and quaternary systems containing B, C and N have not been investigated and thus further study on these systems should be very promising for exploration of new superconductors.

Except for the structural features mentioned above, we must also consider the effect of electron spin. In 1973, Anderson[25] proposed that resonat-

ing valence bond (RVB) state is possible in a geometrically frustrated system. The RVB ground states occur most easily in the triangular antiferromagnetic lattice with $S = 1/2$ and superconductivity is possible in the doped RVB system. Therefore, much attention should be paid to these systems. Doping with electrons (or holes) in an antiferromagnetic Mott insulator can cause the destruction of the local electron spin pairing and introduce the possibility for superconductivity. From the point of view of the chemical bonding, the RVB systems, the doped Mott insulators and the geometrically frustrated systems, may be altogether considered as the 'defective covalent bonding systems'. Therefore, new superconductors might be found in these systems.

It should be mentioned here that having the structural and chemical characteristics is only the essential but not the sufficient conditions for the occurrence of superconductivity. Besides the crystal structure, the occurrence of superconductivity is related with many complex factors such as the electronic structure and lattice vibrations. In addition, the superconducting phase transition must compete with many other phase transitions possibly appearing at low temperatures, such as charge-ordering, magnetic-ordering as well as structural transitions. At present, we can hardly make an ideal design for a new superconductor. However, we hope that the blindness in the exploration of new superconductors could be reduced to some degree with the binary structure model, because it not only specifies the structural characteristics but also provides us with some hints on the chemical compositions of the SAC.

6. Conclusion

In this paper, superconductors were classified into three classes according to the dimension of the covalent-bonding skeleton. The crucial importance of the covalent bonding in superconductors is emphasized and the structural component connected by covalent bond is defined as the superconducting active component. In order to make a superconductor, certain metallic characters must be introduced into the covalent-bond skeleton by electron (or hole) doping. We suggest possible directions to explore new superconductors in the multi-component systems containing nonmetal elements such as B, C, N and O, because these elements are capable of forming partially-metallic covalent bonds.

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