Inner Closed Electron Pairs and Superconductivity Model *

MIKIO FUKUHARA
Research Dept. for Tool Development,
Toshiba Tungaloy,
1-7, Tsukagoshi, Saiwai-Ku, Kawasaki 210, Japan

ABSTRACT

The bonding distances between atoms in five kinds of representative superconductors, Nb_3Sn, $(La,Sr)_2CuO_4$, $YBa_2Cu_3O_{7-\delta}$ $Bi_2Sr_2CaCu_2O_x$ and $Tl_2Ca_2Ba_2Cu_2O_{8+x}$ were calculated and it was found that there were many shrunken bonds along the superconducting current directions. The super-conducting transition temperature increases with the decrease in atomic distance of cations, rather than that of Cu-O. A new approach to theory of high-temperature superconductivity under electronic correlation is proposed, based on the possibility of superelectrons derived from inner filled shells (i.e. superconducting bands) induced by a strong screened attractive electrostatic interaction between an electron and an ion. Delocalization of the pre-existing pairs of electrons causing superconductivity and the transport of superelectrons are discussed in the final section.

INTRODUCTION

It is known that a transition temperature (T_c) of the superconductors such as V_3Si [1], $ErRh_4B_4$ [2], La_{1-x},Ba_xCuO_{3-y} [3], Y-Ba-Cu-Ooxide [4] and the Bach gaardditetramethyl tetraselenaful-valence salts $(TMTSF)_2X$ ($X = PF_6, AsF_6, ClO_4 \cdots$) [5] increases with increasing hydrostatic pressure [6]. Analogous to the pressure effect, it is observed that the T_c of the layer oxides, such as $YBa_2Cu_3O_{7-\delta}$ [7] and $Bi_2Sr_2CaCu_2O_x$ [8], increases as the a and c parameters decrease and the b parameter increases. The enhancement of the T_c is also observed in different morphological substances [9]. A common point of these examples is the presence of an intralattice strain as discussed in an earlier papers [8,10]. If this strain relates to superconductivity, it will be an important factor to consider in search for a superconductor with higher T_c.

---

* This paper is a review of two papers (Ref.(9), (26)) published in Phys.Stat.Sol.(b).

In order to study the relationship between the strain and superconducting behavior, the bonding distances between atoms in five kinds of superconductors such as Nb_3Sn (A-15 type), $(La,Sr)_2CuO_4$ (Popper, K_2NiF_4 type), $YBa_2Cu_3O_{7-\delta}$ (oxygen-deficient triperovskite layer type), $Bi_2Sr_2CaCu_2O_x$ (Aurivillius plus Popper type) and $Tl_2Ca_2Ba_2Cu_3O_{8+x}$ (Aurivillius plus Popper type) are calculated and compared with those of the normal metallic[1] and ionic radii, taking changes in coordination into consideration. Using the fractional change in the interatomic distance found in the structure with reference to the normal radii as an intralattice (or electronic) strain, many different superconducting phenomena are discussed on the basis of strong interaction among electrons.

Following the pioneering work of Bednorz and Müller [11] and the subsequent discovery of superconductivity above liquid-nitrogen temperature in $RBa_2Cu_3O_{7-\delta}$ [12], $Bi_2Sr_2CaCu_2O_x$ [13] and $Tl_2Ca_2Ba_2Cu_3O_{8+x}$ [14], a number of the theories have been proposed to explain this remarkable discovery. The experimental results such as high-energy spectroscopic [15], specific heat [16], Seebeck effect [17] and resistivity measurement studies [18] put severe constraints on the conventional electron-phonon based BCS theory [19]. Recently, there has been a great deal of interest in strong correlations between electrons. Anderson's reasonating valence bond (RVB) mechanism [20], the extended Hubbard (EH) model [21] and the antiferromagnetic fluctuation (AMF) model [22] are representative examples.

A RVB model is based on spin-singlet correlations induced by superexchange between electrons on nearest-neighbor Cu sites. An EH model concentrate on electron correlations induced by the superexchange interaction and weakened by the intersite Coulomb repulsion. An AMF model is proposed as the two-dimensional antiferromagnetic spin correlations induced by spin ordering and trapping of holes. A common point of both RVB and EH models is a mediation of superexchange interaction by excited electron on the oxygen sites in Cu-O-Cu series. Although it seems capable of producing antiferromagnetism in oxides such as MnO [23] and $LaCuO_4$ [24], it is more difficult to imagine that it can be responsible for oxide superconductivity. We also cannot believe the conventional spin-polaron effect such as AMF model in which an electron is coupled to an array of localized Heisenberg spins. The charge density wave (CDW), plasmon, acoustic plasmon and ferromagnetic spin fluctuation models are also proposed as the mediation mechanism in Coulomb interacting among electrons [25]. We do not yet have a completely satisfactory theoretical agreement of either of these

---

1) "Normal metalic" in this study means "non-superconducting".

models.

On the other hand, a new hypothesis based on itinerant paired electrons derived from the inner closed shells was proposed by Fukuhara et al [26]. Since the shells are occupied by the electrons with antiparallel spins in special pair sets of 2, 8, 18, 32 ···, the most important and interesting puzzles which cause the attractive interaction and hence the symmetry property of "*paired electron* " are reasonably settled in beautiful atomic nature, without exchange of virtual phonons between electrons. In other words, these "pre-existing" pairs of electrons cause the superconductivity as soon as they become delocalized as itinerant paired electrons.

In this paper, a new approach to the theory of high-temperature superconductivity under electronic correlation is proposed on the basis of the analysis in previous paper [9]. The central problem of this study is explain why the ground state energy of the paired electrons derived from the completely filled inner shells is reduced at temperature below T_C, and how the paired electrons transport from the shells belonging to one nucleus to the shells of the neighboring atoms when there exists a potential barrier so high that it should not be possible for the paired electrons to escape as itinerant electrons.

CALCULATION OF DISTANCE

The three-dimensional crystal structures in super- and non-superconducting compounds were constructed by the Molecular Editor software package for the Apple Macintosh computer, using the most reliable structural data such as lattice parameters and interatomic distances and bond angles. The coordinate transformation from unit cell coordinates to cartesian ones for structural construction was carried out using Microsoft Excel software package [27].

The atomic distance of two metals in compounds was calculated as the sum of the metallic radii as given in the International Table [28]. The interatomic distance between cation and oxygen in oxides was made on the basis of ' effective' ionic radii by Shannon and Prewitt [29], because changes in the effective ionic radii due to coordination number are larger in magnitude (0.0-0.03 nm) than those due to electronic (magnetic) spin state (~ 0.01 nm), strong anion-anion or cation-cation repulsive force (0.0-0.01 nm) and covalency effects (reasonably constant) [29]. The distance was calculated as the respective sums of the interionic radii of cation and oxygen ion for each coordination number, using the data obtained by Shannon

[29]. The ionic radii for special coordination numbers such as 5, 9, 10 and 14 are interpolated and extrapolated. Furthermore, the cation radius of $La_{0.925}Sr_{0.075}$ in coordination 9 is interpolated with a linear allocation of La and Sr cation radii based on composition.

ATOMIC CONFIGURATION AND BONDING DISTANCES IN THE SUPERCONDUCTING COMPOUNDS

A_3B Compound

The superconductive Nb_3Sn compound having T_c =18.05 K is considered as a representative example of the A-15 type structure. The three-dimensional crystal model of the tetragonal Nb_3Sn is drawn, using the data (a = 0.52933, c = 0.52612 nm) obtained at 5.1 K by R.Mailfert *et al*. [30]. The model is shown in Fig. 1.

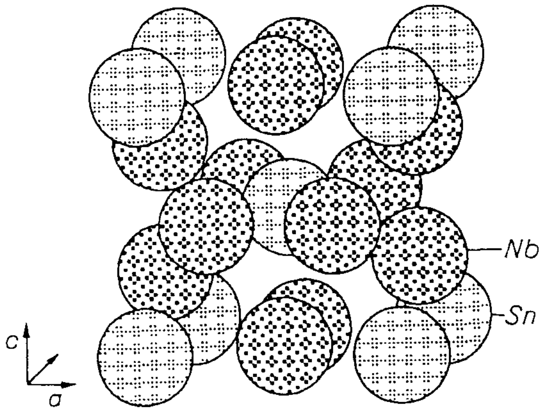


Figure 1. Three-dimensional crystal model of the tetragonal Nb_3Sn as a representative example of the A-15 type compound. The structure was drawn from data by [30].

The atomic distances between Nb and Sn atoms are presented in Table 1 together with the data for the interatomic distances in metallic crystals [28]. The atomic distances of Nb atoms along <001>, and <100> or <010> are considerably smaller than the sum of the two Nb metal radius (8.0 and 7.4 % in reduction, respectively). This means that Nb atoms in the superconducting lattice are forced to squeeze together compared with Nb atoms in a normal metallic lattice. Therefore, it is considered that the intralattice strain accumulates between Nb atoms, and it may contribute to superconductivity. Indeed, Ekin [31] has reported the effect of strain on the superconducting critical current of Nb_3Sn; that is, the effect of 0.05

TABLE 1
Atomic bonding distances among Nb and Sn atoms in the tetragonal Nb_3Sn lattice

Bonding atoms	Bonding direction	Distance between atoms (10^{-1} nm) A	Interatomic distance (10^{-1}nm) B	Percent Shrinkage $\frac{A-B}{B}$x100 (%)
Nb-Nb	<001>	2.631	2.858	- 7.96
	<100><010>	2.647		- 7.40
	[112]	3.228		+12.95
	[211]	3.238		+13.30
Nb-Sn	[120]	2.959	2.940	+ 0.65
	[012]	2.944		+ 0.14

% strain at low strain fields is to degrade the critical current by only 0.3 % due to relief of an intralattice strain.

Since the maximum shrinkage of Nb atoms in the non-superconducting cubic lattice at 50.0 K is also 7.6 %, it is difficult to explain the presence of superconductivity on the basis of the reduced distance of Nb atoms alone. Metallic conductivity in compounds with shrunken bonds may follow the Mott model [32] discussed later. Superconductivity is probably related to the spontaneous tetragonal strain in the Nb sublattice as deduced from studies of the lattice-dynamical phase transition in Nb_3Sn by G.Shirane *et al.*[33], and sublattice distortion in V_3Si by Patel *et al* [34].

It is also observed that the T_c of the A15 niobium alloys increases still more as the a parameter, namely, interatomic distance between Nb atoms decreases due to substitution of other lighter element in place of Sn [35]. From this point of view, the high T_c superconductor consisting of A_3B compound calls for the tetragonal lattice with large lc/al ratio and rigid bond between A atoms.

$(La,Sr)_2CuO_4$

Next, $(La_{0.925},Sr_{0.075})_2CuO_4$ with a T_c of 35 K and rhombicity $^{2)}$ of 0.0024 nm is selected as a representative example of K_2NiF_4 (Popper) structure. Figure 2 shows the three-dimensional crystal model (a half unit cell) of the superconductive orthorhombic phase proposed on the basis of the neutron powder diffraction

---

2) Rhombicity is defined as the difference between a and b parameters in orthorhombic phase.

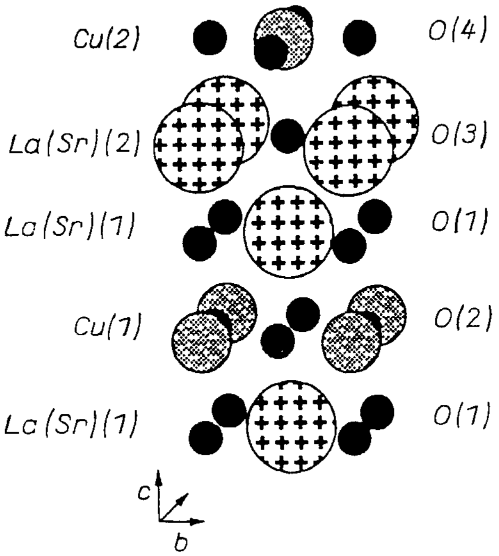


Figure 2. Three-dimensional crystal model (half unit cell) of the orthorhombic $(La_{0.925},Sr_{0.075})_2CuO_4$ having T_c of 35 K and rhombicity of 0.0024 nm as a representative example of K_2NiF_4 (Popper) structure. The structure was drawn from data by [36]

analysis at 7 K by François *et al* [36]. It is characterized by the La(Sr) atom with 9-coordination between the rock-salt-type La(Sr)O layer and the perovskite layers. The atomic bonding distances between La(Sr), copper and oxygen atoms are presented in Table 2, where the precise bonding direction between metal cation and oxygen anion cannot be precisely described because the CuO_6 octahedrons are tilted by about 3° about one of pseudotetragonal a axes [36].

The distances of Cu-O in the basal-plane squares and La(Sr)-O along the c axis are shorter than their normal metallic and ionic bonding ones; that is, these atoms are forced to shrink. In general, the octahedron units in perovskite-like materials tend to have strong internal bonding, resulting in short interatomic distances [37]. However, the short bonds are not continuous in the perovskite layer of the oxides such as ferro-electrics, as is discussed later. In the cuprate perovskite of the La oxide, the intralattice strain accumulates both between Cu and oxygen, and also between $(La_{0.925},Sr_{0.075})$ and oxygen atoms. This may be related to the superconductivity in this Popper type structure, as it does between Nb atoms in Nb_3Sn. However, since the La(Sr)-O bond is not continuous along the c axis, the superconducting electrons seem to flow along the square planar arrangement perpendicular to the c axis [38]. In a superconducting oxide solid solution $(La_{1-x}(Ba,Sr,Ca)_x)_2CuO_{4-\delta}$, it is also reported that T_c increases as the a parameter,i.e, the Cu-O bond in the basal plane, decreases [39].

TABLE 2
Atomic bonding distances among La(Sr), Cu and O atoms in the orthorhombic $(La_{0.925},Sr_{0.075})_2CuO_4$ lattice.

Bonding atoms	Bonding direction	Coordination number		Distances between atoms (10^{-1} nm) A	Interatomic Distances (10^{-1} nm) B	Percent Shrinkage $\frac{B-A}{B}$ x100 (%)
		La (Sr)	O			
$La_{0.925}Sr_{0.075}$ (2) - O(3)	[110]	9	10	2.576	2.6429	- 2.53
				2.724		+ 3.07
				2.891		+ 9.39
$La_{0.925}Sr_{0.075}$ (2) - O(1)	[001]		9	2.363	2.6349	- 10.32
$La_{0.925}Sr_{0.075}$ (2) - O(4)	[011]		14	3.067	2.6649	+ 15.09
				3.055		+ 14.64
		Cu	O			
Cu (1) - O (2)	[100]	6	14	1.8823	2.188	-13.96
	[010]			1.8908		- 13.58
Cu (1) - O (1)	[001]		10	2.408	2.166	+ 11.17
$La_{0.925}Sr_{0.075}$ (2) - $La_{0.925}Sr_{0.075}$ (2)	[100]			3.7646	3.81125	- 1.22
	[010]			3.7816		- 0.78
	[001]			4.816		+ 26.36
$La_{0.925}Sr_{0.075}$ (2) - $La_{0.925}Sr_{0.075}$ (1)				3.564		- 6.49
$La_{0.925}Sr_{0.075}$ (2) - Cu (2)	[100]			3.557	3.1836	+ 11.72
	[010]			3.579		+ 12.41

Although earlier papers have reported that the superconducting $(La_{1-x}, (Sr,Ba)_x)_2 CuO_{4-y}$ phase is tetragonal, it is practically orthorhombic. Fujita *et al.* [40] have reported that the T_c is directly under the tetragonal-orthorhombic transition temperature, T_d from phase diagram of transition temperatures T_d, and T_c vs composition in $(La_{1-x},Ba_x)_2CuO_{4-y}$. More recently, several groups have observed superconductivity in the unsubstituted orthorhomic phase La_2CuO_{4-x} at temperature (4 -16 K) just below the metal-to-insulator phase transition [41]. This means that the lattice distortion due to rhombicity needs an accumulation of the intralattice strain.

$YBa_2Cu_3O_{7-\delta}$

The crystal model (half unit cell) of orthorhombic $YBa_2Cu_3O_{6.96}$ with high T_c (about 93 K) and large rhombicity (0.0066 nm) is shown in Fig. 3. The structure was

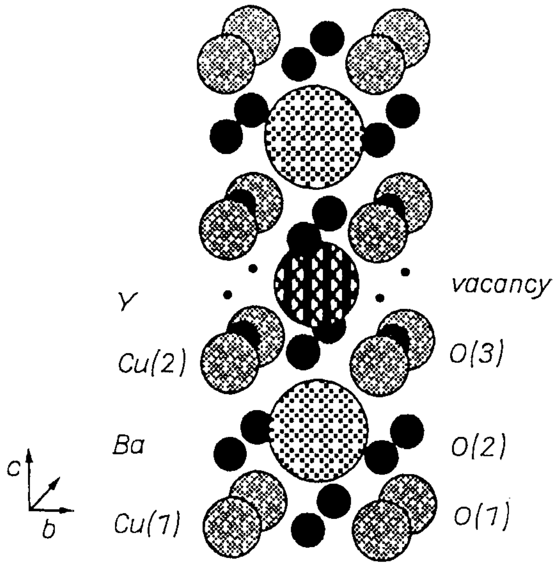


Figure 3. Three-dimensional crystal model (half unit cell) of the orthorhombic $YBa_2Cu_3O_{6.96}$ with T_c of about 93 K and rhombicity of 0.0066 nm as a representative example of $RBa_2Cu_3O_x$. The structure was drawn from data by [42].

determined at 8 K by Johnston *et al.* [42], using powder X-ray and neutron diffraction methods. Table 3 presents the atomic bonding distances among the Y, Ba, Cu and O atoms in this crystal in comparison with normal metallic and ionic ones, where it is found that many shrunken bonds, defined as the intralattice strain, exist in this oxide. This means that these atoms are forced to squeeze into the lattice skeleton modified by the strong bonds associated with the affinity of II-III group elements for oxygen, as discussed in a previous paper [9]. The intralattice strain accumulating in the surroundings of the shrunken bonds may lead to the superconducting state. Horn *et al.*[43] have reported a possibility that the superconductivity in $YBa_2Cu_3O_7$ induces a small distortion ($\leq 2 \times 10^{-4}$) in the unit-cell volume, whereas there is no anomaly in the unit cell volume or in the in-plane area. If so, since the percent shrinkage of the shrunken bonds such as Ba-Ba and Cu(2)-O along the a axis are larger than those of the b axis, the superconducting current along the a axis seems to be predominant in the crystal. Current along the b axis is also possible, but not as high as that along the a axis. On the other hand, the current along c axis is very small because the shrunken bonds such as Ba-Y and Cu(1)-O are not continuous in this direction. These discussions agree with the experimental data for single crystals [44].

Since the percent shrinkage of the Cu(2)-O bond along the a axis in the tetragonal pyramid is relatively large as well as that of Cu-O bond along the a axis in $(La_{0.925},Ba_{0.075})_2CuO_4$, it is clear that tetragonal and octahedral coordinations

TABLE 3

Atomic bonding distances among Y, Ba, Cu and O atoms in the orthorhombic $YBa_2Cu_3O_{6.96}$ lattice.

Bonding atoms	Bonding direction	Coordination number		Distances between atoms $(10^{-1} nm)$ A	Interatomic distance $(10^{-1} nm)$ B	Percent Shrinkage $\frac{A-B}{B}$ x 100 (%)
		Ba	O			
Ba - O(2)	[110]	10	12	2.737	2.968	- 7.78
Ba - O(1)	[011]			2.877		- 3.07
Ba - O(3)	[101]			2.948		- 0.67
	[011]			2.960		- 0.27
		Cu	O			
Cu(1)-O(1)	[010]	4	10	1.939	2.056	- 5.69
Cu(1)-O(2)	[001]		12	1.845	2.068	- 10.78
Cu(2)-O(3)	[010]	5	12	1.957	2.098	- 6.72
	[100]			1.923		- 8.10
Cu(2)-O(2)	[001]			2.294		+ 9.34
		Y	O			
Y - O(3)	[111]	8	12	2.406	2.463	- 2.31
				2.372		- 3.69
Ba-Ba	[100]			3.8127	4.347	- 12.29
	[010]			3.8780		- 10.79
	[001]			4.3095		- 0.86
Ba -Y	[001]			3.678	3.9505	- 6.89
Y - Y	[100]			3.8127	3.554	+ 7.28
	[101]			3.8780		+ 9.12
Ba- Cu(1)				3.471	3.4515	+ 0.56
Ba- Cu(2)				3.373		- 2.27
Y- Cu(2)	[111]			3.200	3.055	+ 4.75

about the copper cation in these oxides play an active role in superconductivity, as pointed out in many papers [45]. However, from the viewpoint of Cu-O coordination alone, it is difficult to explain a large enhancement of T_c in $RBa_2Cu_3O_x$, compared with $(La,M)_2Cu_4O_x$ (M: Ba, Sr and Ca) oxide. It can be speculated that the superconductivity in the $R_nBa_2Cu_3O_x$ is essentially based on the double or triple shrunken (or compressive) bondings of Ba-Ba and Cu(2)-O atoms along the a axis. In practice, the T_c of $YBa_2Cu_3O_{7-x}$ increases as the a parameter, namely the interatomic distance of Ba decreases [46]. Therefore, the alkaline earth cations such as Ba, having large ionic radii, are desirable for compressive atomic bonding, i.e, enhancement of T_c.

In order to clarify this point, further investigation such as barium isotope substitution is needed. Bourne *et al.*[47] have recently reported that substitution of the isotopes ^{138}Ba for ^{135}Ba and ^{65}Cu for ^{63}Cu in $YBa_2Cu_3O_7$ has little or no effect on T_C. However, since they have not paid attention to an influence of oxygen deficiencies on T_C, it is difficult to support their experimental results because the decrease in T_C of $YBa_2Cu_3O_{7-\delta}$ is caused by the oxygen deficiencies, as pointed out by many research groups [7,42,48].

$Bi_2Sr_2CaCu_2O_x$

To the authors' knowledge, although the crystal structures of an oxide superconductor having high T_C (~107 K) in Bi-Sr-Ca-Cu-O system are proposed by various research groups, all models are not complete; for some of them there is no description of the Bi_2O_2 layer, and there is a misunderstanding of Bi tetragonal arrangement, and ignorance of Sr(Ca) coordination. Fukuhara *et al.* [8] proposed that the structure of $Bi_2Sr_2CaCu_2O_x$ consists of an Aurivillius-like phase having two perovskite layers interleaved with a Popper-like phase. The three-dimensional model (half unit cell) of an orthorhombic crystal with high T_C (107 K) and large rhombicity (0.155) is shown in Fig. 4. The positional parameters,especially the z

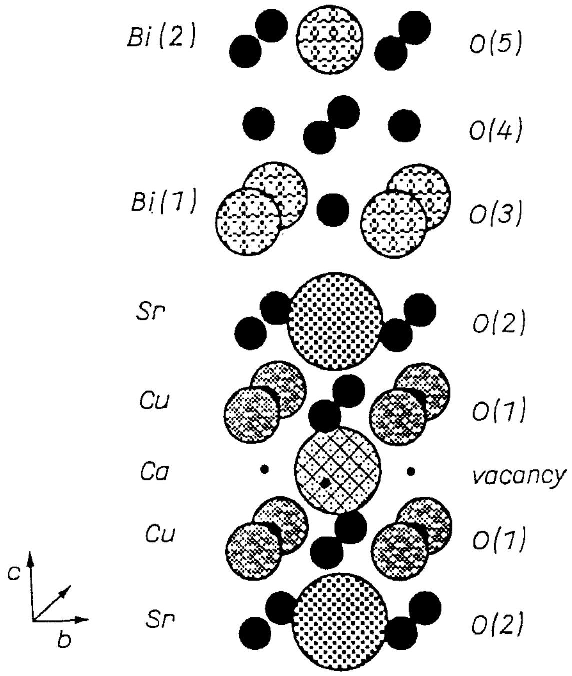


Figure 4. Three-dimensional crystal model (half unit cell) of the orthorhombic $Bi_2Sr_2CaCu_2O_x$ with T_C ~107 K and rhombicity of 0.0155 nm. The structure was drawn from data by [8] and [49].

coordination of each atom are referred to the metal-oxygen distances at room temperature determined by Tarascon *et al* [49], because their c parameter (3.05 nm) is very close to that of data (c = 3.06 nm) contained in previous paper [8]. The structure is characterized by the two strontium and oxygen atoms with a 9-coordination between the Bi_2O_2 and the perovskite layers.

The atomic bondings among Bi, Sr, Ca, Cu and O atoms are presented in Table 4. There are many shrunken bonds in this structure comparable to those of

TABLE 4
Atomic bonding distances among Bi, Sr, Ca, Cu and O atoms in the orthorhombic $Bi_2Sr_2CaCu_2O_x$ lattice

Bonding atoms	Bonding direction	Coordination number		Distances between atoms (10^{-1} nm) A	Interatomic distance (10^{-1}nm) B	Percent Shrinkage $\frac{A-B}{B}$ x 100 (%)
		Bi	O			
Bi(1) - O(4)	[101]	9	9	2.909	2.598	+ 11.97
	[011]			2.945		+ 13.36
Bi(1) - O(3)	[110]	9	9	2.698		+ 3.85
Bi(1) - O(2)	[001]			2.969		+ 14.28
		Sr	O			
Sr - O(3)	[001]	9	9	2.969	2.720	+ 9.15
Sr - O(2)	[110]	9	10	2.698	2.728	- 1.10
Sr - O(1)	[101]	9	12	2.863	2.740	+ 4.49
	[011]			2.900		+ 5.84
		Cu	O			
Cu - O(2)	[001]	5	10	2.159	2.086	+ 3.50
Cu - O(1)	[100]	5	12	1.880	2.098	- 10.39
	[010]			1.935		- 7.77
		Ca	O			
Ca - O(1)	[101]	8	12	2.595	2.568	+ 1.05
	[011]			2.633		+ 2.53
Bi(1) - Bi(1)	[100]			3.761	3.111	+ 20.89
	[010]			3.870		+ 24.40
Bi(1) - Sr				4.012	3.7065	+ 8.24
Sr - Ca	[001]			3.945	4.1245	- 4.35
Sr - Sr	[100]			3.761	4.32	- 12.94
	[010]			3.870		- 10.42
Ca - Ca	[100]			3.761	3.947	- 4.71
	[010]			3.870		- 1.95

$YBa_2Cu_3O_{7-\delta}$. The further structure analysis at low temperature below T_c will make all the shrinkage percents increase still more. If the reduction in atomic radius (intralattice strain) is related to superconductivity to the above mentioned oxides, then the superconducting current is predominant on the basal plane, especially in the a axis direction. However, the current along the c axis without continuous shrunken bond may be impossible. These discussions agree favorably with the experimental data obtained from the single crystal $Bi_2(Sr,Ca)_{3-d}Cu_2O_x$ [50].

As can been seen from Fig.4, an apex Bi atom of the tetragonal pyramid in the bismuth oxide layer forms a shortened bond to an apex oxygen of the CuO_6 octahedron or CuO_5 tetrahedral pyramid in the perovskite layer, as if it is an hour glass.

If the oxygen sites above and below the bismuth oxide layer (forming an hour glass) are vacant as assumed by Takayama-Muromachi *et al* [51]; or the Bi atoms are coordinated as an Aurivillius type structure (forming an umbrella) as proposed by various research groups, it would be difficult for Bi and Sr atoms to draw near one another due to electrostatic repulsion among neighboring cations. The existence of an oxygen atom with 9 coordination between Bi_2O_2 and the perovskite layers decreases the distance between Bi atoms, namely a and b parameters due to ionic attraction between Bi and oxygen atoms. As a result, the atomic distance between Sr cations also decreases, and it leads possibly to superconductivity. The Bi(1)-O(3) bond therefore seems to play a key role in superconductivity of $Bi_2Sr_2CaCu_2O_x$. Thus, if the oxide will consist of the perovskite having the complete CuO_6 octahedron without oxygen deficiencies, further enhancement of T_c will be expected as pointed out in the previous paper [8]. In the case of $RBa_2Cu_3O_{9-\delta}$, the more the number of oxygen anions surrounding the metal cations such as Ba and R, the more T_c will increase, as pointed out by many research groups [7,42,48].

From these discussions, it is considered that the large enhancement of T_c in $Bi_2Sr_2CaCu_2O_x$ can be explained by the shrinkage and the large rhombicity. The rhombicity (0.014-0.020 nm [8]) in $Bi_2Sr_2CaCu_2O_x$ is two to four times as large as that (0.005 [Ref.52]-0.006 [Ref.42] nm) of $YBa_2Cu_3O_{7-\delta}$. The relationship between T_c and rhombicity in all of the above mentioned compounds is shown in Fig. 5. Since the rhombicity of oxides decreases as the amount of oxygen deficiencies increases, depending on sintering and annealing conditions, the data of the crystals having the largest rhombicity are selected. As can been seen from Fig. 5, T_c increases as the rhombicity increases. Thus the large rhombicity seems to play an important role in the construction of continuous shrunken bonds.

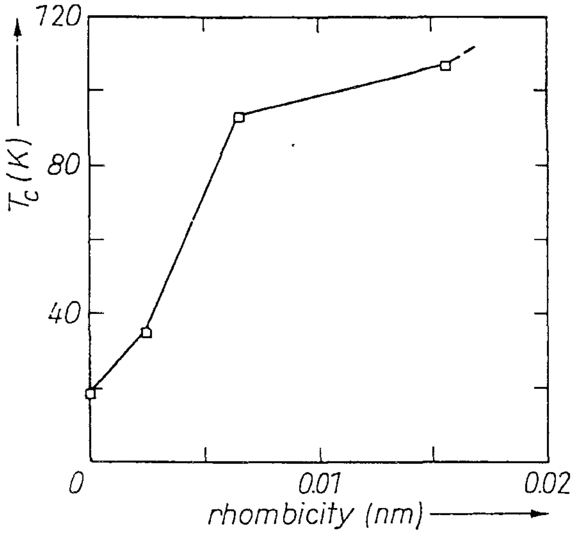


Figure 5. Relationship between critical temperature (T_c) and rhombicity

Since all the orthorhombic phases of the layered superconducting oxides mentioned above have higher densities than the tetragonal forms [8,34,42,49], the large rhombicity contributes to the formation of many shrunken bonds, i.e, enhancement of T_c. It should be noted that White *et al.*[53] and Serebrynaya *et al.*[54] showed that the high-temperature, high-pressure phases of layered tetragonal PbO and SnO, respectively are the orthorhombic modifications that have higher densities than the tetragonal forms. Hence, by analogy it is inferred that these layered structures which havie large rhombicity tend to have higher density without ultra high pressure because of the existence of a large number of oxygens.

$Tl_2Ca_2Ba_2Cu_3O_{8+x}$

It is reported that $Tl_2Ca_2Ba_2Cu_3O_{8+x}$ is a superconductor with the highest T_c of ~ 125 K as of March 1989 [55]. The three-dimensional crystal model (half unit cell) is drawn in Fig. 6, using tetragonal crystallographic data determined from single-crystal (T_c = 122 K) X- ray diffraction at room temperature by Torardi *et al*[56]. The bonding distances among Tl, Ca, Ba, Cu and O atoms are presented in Table 5, together with the calculated values for normal metal and ionic bonding. The continuous thirty-six shrunken bonds such as Ba-Ba and Cu-O per unit cell exist on the basal plane perpendicular to the c axis. If these bonds are related to superconductivity as has been suggested for the oxides mentioned above, the current on the basal plane will be predominant.

In order to make clear a reason for the highest T_c in $Tl_2Ca_2Ba_2Cu_3O_{8+x}$, maximum atomic shrinkage in shrunken cation and Cu-O bonds of five compounds

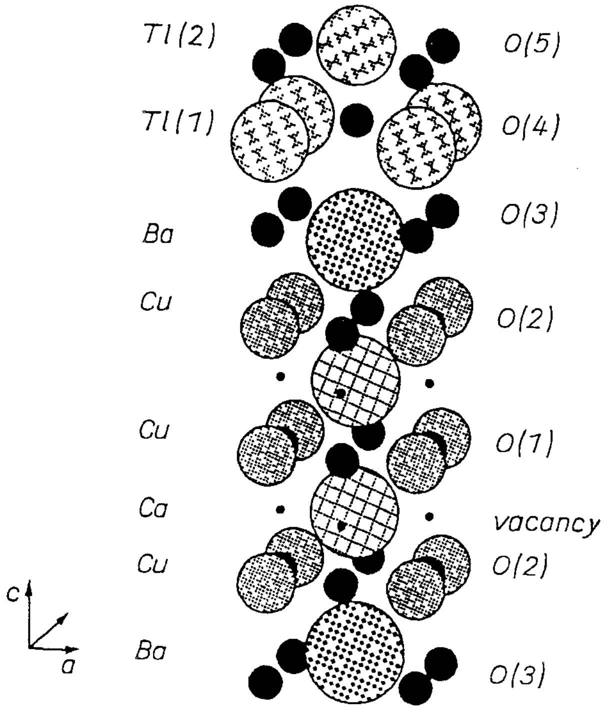


Figure 6 Three-dimensional crystal model (half unit cell) of the orthorhombic $Tl_2Ca_2Ba_2Cu_3O_{8+x}$ with highest T_c of 122 K. The structure was drawn from data by [56]

mentioned above are plotted as a function of T_c (Fig. 7). T_c increases as the percent shrinkage of cations increases. A negative slope of the Cu-O bond shows that the shrunken Cu-O bonds do not depend directly on the higher T_c in oxides with many Cu-O layers.

In spite of higher T_c of the Tl oxide, the maximum shrinkage (11.4 %) between Ba cations is smaller than that (12.9 %) of the Bi oxide. The percent shrinkage will increase still more if the superconducting phase of $Tl_2Ca_2Ba_2Cu_3O_{8+x}$ is orthorhombic at low temperature (below 122 K), although the crystal structure has been reported as tetragonal at room temperature up till now. In practice, the Tl oxide crystal used by Torardi *et al.*[56] seems to be incomplete; probably because of an oxygen deficiency. Therefore, discussions about the Tl oxide must be limited at present.

In addition, it is suggested that the Ba ion with its large ionic radius is desirable for the occurrence of superconductivity. Indeed, all the atomic radii of cation elements such as Ba, Sr, La, Y and some of the rare earth elements which constitute superconducting oxides, are above 0.17 nm [57] except for Cu. These cations are

TABLE 5

Atomic bonding distances among Tl, Ca, Ba, Cu and O atoms in the tetragonal $Tl_2Ca_2BaCu_3O_{8+x}$ lattice

Bonding atoms	Bonding direction	Coordination number		Distances between atoms (10^{-1}nm) A	Interatomic distance (10^{-1}nm) B	Percent Shrinkage $\frac{A-B}{B}$ x 100 (%)
		Tl	O			
Tl(1) - O(4)	[110]	6	9	2.737	2.308	+ 18.59
Tl(1) - O(3)	[001]		10	2.198	2.316	- 5.09
		Ca	O			
Ca - O(2)	[101]	8	10	2.427	2.556	- 5.05
		Ba	O			
Ba - O(3)	[110]	9	9	2.768	2.898	- 4.49
Ba - O(2)	[101]		12	2.815	2.918	- 3.53
Ba - O(1)	[001]		14	2.767	2.928	- 5.50
		Cu	O			
Cu - O(2)	[100]	5	12	1.926	2.098	- 8.20
Cu - O(1)	[001]		10	2.479	2.086	+ 18.84
Tl(2) - Tl(1)				3.850	3.362	+ 14.52
Tl(1) - Tl(1)	[100]			3.850		+ 14.52
Ca - Ca	[001]			3.321	3.947	- 15.86
	[100]			3.850		- 2.46
Ca - Cu				3.134	3.2515	- 3.61
Ca - Ba	[001]			3.533	4.147	-14.81
Ba - Ba	[100]			3.850	4.347	-11.43

all electropositive ones which help in the formation of superconducting oxides and stabilize higher formal oxidation states for transition elements [58]. This is actually an indirect effect, as pointed out by Sleight [58]. Copper alone seems to form as small chains of Cu-O in superconductvity.

DERIVATION OF SUPERELECTRONS

Judging from the data discussed above, the shrunken bond chains are essential for

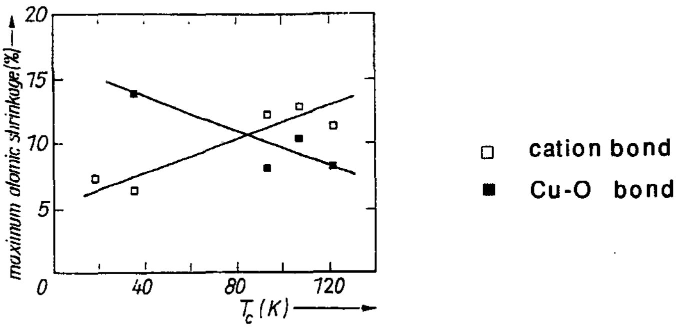


Figure 7 Relationship between T_c and maximum atomic shrinkage in shrunken cation and Cu-O bonds of five compounds

high-temperature superconductivity. To account for the effect of oxygen in oxide superconductors, it is proposed that the following parameter τ for a superconductive compound consisting of $(I_A, II_B, III_C, IV_D, V_E, VI_F, VII_G, VIII_H)(C_X, N_Y, O_Z)_W$ of group I to VIII elements be used:

$$\tau = \frac{\text{VEC of anions}}{\text{VEC of cations}} \qquad (1)$$

because the properties of the compound can be determined by adjusting the height of the Fermi level to the valence electron concentration(VEC) first proposed by Bilz [59]. The VEC has been defined as follows [60]:

$$\text{VEC} = 1A+2B+3C+4D+5E+6F+7G+8H+4XW+5YW+6ZW\ , \qquad (2)$$

where A, B, C, D, E, F, G, H, X, Y and Z are molar fractions, W is the atomic ratio of non-metal to metal, X+Y+Z=1. The τ values of the representative oxide superconductors reported in earlier papers [61,62,63,64] have been calculated and presented in Fig. 8 as a function of T_c. The data used have been taken exclusively from literature on oxides with refined compositions and T_c . Unfortunately, very little that has been written on this subject proved usable.

As can been seen from Fig. 8, T_c can be expressed as $T_c = 0.268 * e^{1.31\ \tau}$. Therefore, it is expected that a room temperature (300 K) superconductor would be an oxygen excess compound (peroxide) with $\tau = 5.4$. This means that the more oxygen anions surround the cations, the more the radii of cations shrink to lessen the electrostatic repulsion between cations like ultra-high pressure effect.

Indeed, in the case of $Bi_2Sr_2CaCu_2O_x$, the percent shrinkage of Sr-Sr bonds along the a axis is 12.94 %, and the atomic volume in reduction is 34.01%. This reduction owes its existence to the oxygen between Bi(1)-Bi(1), as described above.

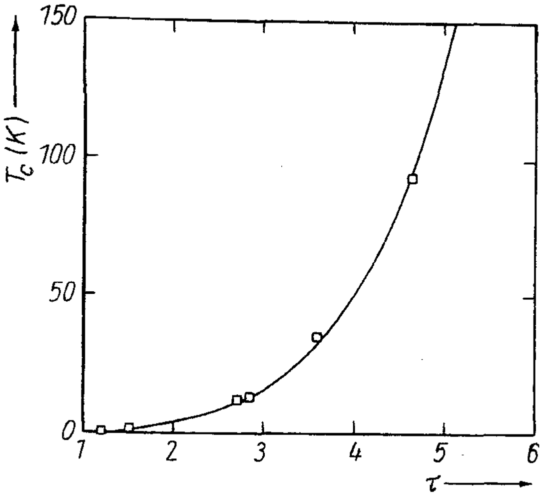


Figure 8. Relation between T_c and parameter τ ; $NbO_{1.0}$[61] (T_c=1.2K, τ = 1.20), $TiO_{1.0}$[62] (T_c=2.3K, τ =1.50), $Li_{1.05}Ti_{1.95}O_4$ [63] (T_c = 12.0, τ= 2.712), $BaPb_{0.7}Bi_{0.3}O_3$ [64] (T_c = 13K, τ = 2.857), $La_{1.85}Sr_{1.15}O_4$ [34] (T_c = 35K, τ =3.609) and $YBa_2Cu_3O_{6.96}$[41] (T_c=93K, τ =4.640). T_c can be expressed as T_c= 0.268 x exp (1.31τ)

Since the nucleus has very small dimensions ~10^{-6} -10^{-5} nm as compared with atomic dimensions ~0.1nm[65], all inner orbiting electrons of shrunken atoms in the superconducting compounds mentioned above are probably forced to press toward to the nucleus. Hence, we can visualize two models of the electronic state; one is a localized electron model around the nucleus and the other is a condensed one keeping ordinary electronic configuration. It is probably the latter, because of the existence of an extremely small energy gap (~ 10^{-8} eV per atom [66,67]), and relatively small carrier density ~ $10^{21}/cm^3$ in the oxide superconductors [68,69].

The Pauli exclusion principle prevents multiple occupancy, so that a crystal in general can be an insulator only if the number of valence electrons in a primitive cell of the crystal is an even integer. Exceptions must be made, however, for electrons in crystal lattices extremely compressed, and in tightly bound inner shells which cannot be treated by the band theory [70]. In the condensed electron state under intensive compression below T_c, the electrostatic energy of the system changes, and, consequently, the charge distributions in inner orbiting electrons consisting of closed shells may overlap. The electron distribution can overlap only if accompanied by a partial promotion of electrons to an unoccupied lower energy state of the atom because the valence electrons with high energy of the metal cations have already been consumed in the formation of the rigid skeleton of the superconducting oxide, and there are no unoccupied high energy states. Thus it is considered the electron overlap decreases the total energy of the system under ultra-high pressure due to existence of excess oxygen, and leads to superconductivity. The driving force of the current is not the electric field, but an electrostatic attraction between electrons and ions. New electrons attributing to superconductivity increase with the decrease of temperature as if excessive electrons are created from the inner filled bands. These physical features are depicted in Fig. 9, on the basis of the band theory, using $Bi_2Sr_2CaCu_2O_x$ as an example.

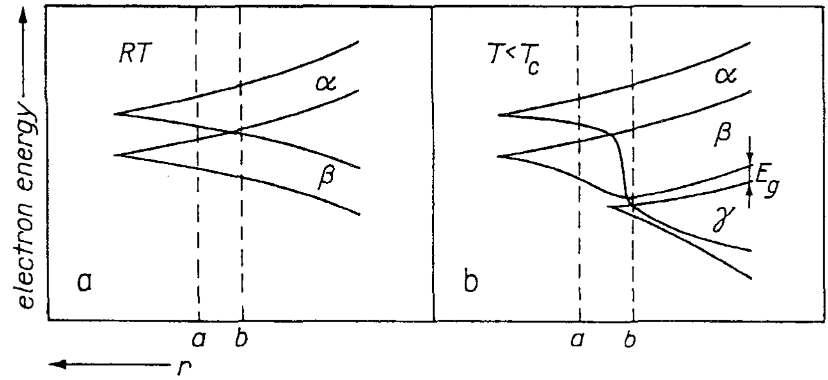


Figure 9. Electron energy as a function of interatomic spacing for compound having the squeezed atoms. Showing an empty zone (α) and full zones (β metallic conduction, and γ superconduction) varing with the interatomic distance *b*.

At room temperature, as both Sr atoms in the oxide are attracted due to the interaction of Bi(1)-O(3), decreasing the radius from its equilibrium value a in its insulating state, it would be expected that both full and empty bands for metallic conduction would overlap below the radius of b leading to a metallic conducting state (Fig, 9(a)). This is the Mott transition model [32] from insulator to metal, which estimates a discontinuous increase in the number of free electrons under a screened Coulomb interaction. Metallic conductivity above T_c in the oxide superconductors mentioned above therefore can be explained by this model. In practice, the Cu-O bands in all cuprate oxides may be responsible for metallic conductors.

On the other hand, at temperatures below T_c (Fig. 9(b)), the empty band for superconduction widens abruptly toward the lower energy levels below b and overlaps with the inner shell electron band; and thereafter, the number of superelectrons3) increases uniformly. In Fig. 9, E_g is the energy gap from the superconducting to the metallic conducting state. This physical meaning is intrinsically different from the energy gap in semiconductivity. If the electron is considered to be composed of two interpenetrating fluids (the two-fluid model); - of superelectrons derived from d orbits for an example and normal itinerant electrons - superconductivity may occur without an actual energy gap. Recent specific heat studies of high-T_c superconductors have suggested a possibility of superconductivity with the energy gap [71].

Although it is thought that an electron deriving from the inner orbits is a kind of itinerant electron, there are differences between the electrons in condensed electron state at very low temperatures and the electrons in freely mobile electron state (e.g. in semi-conductors) at room temperature. It has been believed that *Cooper pairs*, by an exchange of suitable virtual phonon, consist of two itinerant electrons with opposite moment vectors *k* and with opposite spin [72]. Moreover, the origin of the itinerant electrons in superconductivity is not clear in the literature as far as is known. These phenomena can be viewed in many different superconductive effects.

Phonon effect

Since the inner orbit electrons combine even more strongly with a nucleus with a large positive charge comparable to those of normal conducting atoms, it is thought that lattice vibration is strongly suppressed; the contribution of phonon may therefore decrease considerably. This can be assumed from the very low thermal conductivity in superconductors [73,74], the temperature-independent Seebeck effect at super-conducting temperature region in $(La_{0.95},Sr_{0.05})_2CuO_4$ [75] and $YBa_2Cu_3O_{9-x}$ [76] and the sharp entropy drop below T_c [77,78] in perfect analogy with what occurs in ordinary liquid helium (the λ anomaly)[79]. The decrease in phonon frequency can also be estimated with the increasing of atomic shrinkage (%) in shrunken atoms. Therefore, it seems to be clear that this process must involve only the free electrons of the superconductor, because this entropy vibration comes from the electronic specific heat alone and not from the lattice contribution accounted for in Debye's law, as is also pointed out by Careri [80]. The electrons are probably able to move without mediation of phonon. Furthermore, it can be expected that the mean free path of the superelectrons is very short (perhaps just an interatomic spacing) compared with that (~ 10^8 interatomic ones) of a *free electron Fermi gas* in normal electrons at low temperatures [81]. Indeed, the smallest values of the coherent length (ξ ~0.36 nm) are in good agreement with the

---

[3] *Superelectron* is defined as the coupled electron pairs with twice the charge and mass of an electron [132].

mean free path [82]. Thus, the pairing interaction in the oxides is probably not mediated by phonons but by another mechanism; strong interaction among electrons is also predicted.

diamagnetic effect

Diamagnetism results from slight perturbations of the orbital motions of each electron in the materials due to the force which each experiences when moving in a magnetic field [83]. In nature, it is conspicuous in elements such as He, Ne, Ar, Zn and Cd, which are characterized by closed electron shell structures which have neither total orbital angular magnetic moment,*l*, nor total spin angular moment,*s*. The magnetic susceptibility (χ) of normal metals such as Zn and Cd is 10^{-5} ~10^{-4} [H/m] [84]. On the other hand, perfect diamagnetism in superconducting materials has a susceptibility of the order of one [H/m] [85]. To our knowledge, the extremely large difference in susceptibility between normal- and super-conducting states has not been completely explained yet.

As mentioned above, in oxide superconductors, the valence electrons of metal atoms combine with those of oxygens to form the rigid oxide skeleton, and, consequently, atoms having a large radius in the oxide are forced to squeeze; the electrons and their orbits are also forced to condense toward the nucleus. Since the condensed orbits keep the electronic shell-structures of the inert gas atoms, the electrons in the inner orbits become extremely susceptible to applied magnetic fields because atomic diamagnetism depends only on the effective radii of the electronic orbits. According to the classical theory of Langevin, the susceptibility per gram atom is given by the formula [86]:

$$\chi = -\frac{Ne^2}{6\,mc^2}\,\Sigma\, r_i^2 \qquad (3)$$

where*e* and m refer to the charge and mass of the electron respectively, c the velocity of light, N to Avogadro's number, and r_i^2 to the sum of the mean square radii of the orbit of *i* -th electron projected perpendicular to the direction of the applied field. Thus, perfect diamagnetism cannot be induced until the external magnetic flux begins to react with the inner orbit electrons. This repulsive force can be explained by Pauli's exclusion principle. Hence, the feeble diamagnetic susceptibility in elements having "spin paired" electrons can be regarded as the result of the screened effect exerted by the inner closed shell.

Isotope effect

Measurements of the transition temperature on different *isotopes* of the same element showed that T_c is a function of the isotope mass. The experimental results within each series of isotopes may be summarized by a relation of the form [87]

$$M^{\alpha} T_c = \text{constant} \tag{4}$$

where M is the isotopic mass and α is usually close to 0.5 for the full isotope effect. This isotope effect suggests that the mechanism underlying superconductivity must involve the properties of the lattice, in addition to those of the electron. Since the frequency of ionic vibrations for very simple oscillators is proportional to $M^{-1/2}$ [88], until now it has been believed that superconductivity is intimately connected with electron-phonon interactions.

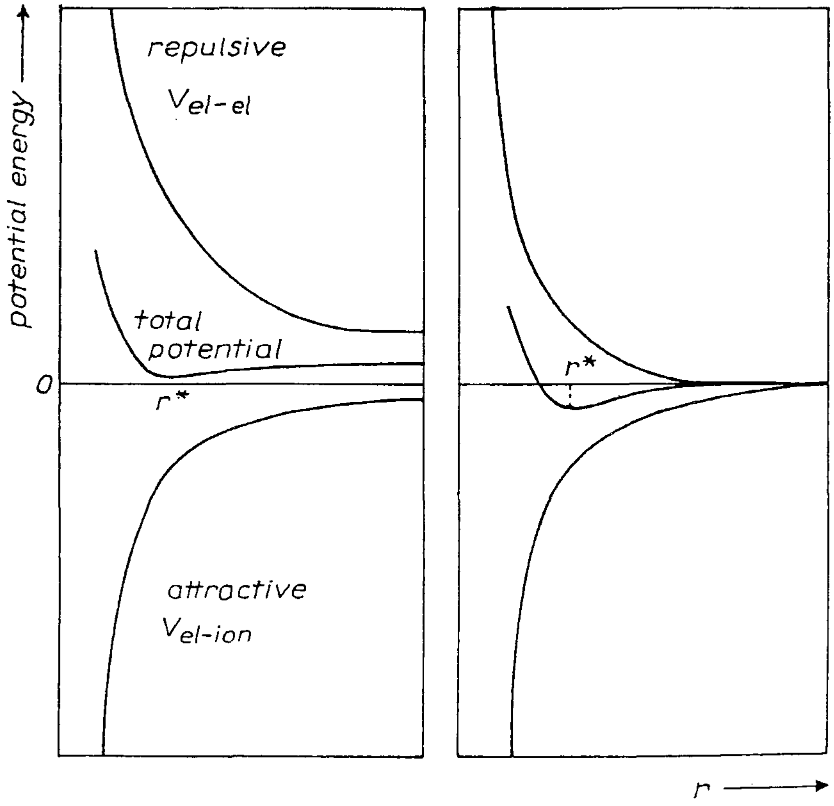
However, depending on the number of neutrons in the nucleus, the atomic radii of the isotopes change, and hence the state of the condensed electron in shrunken atoms modulates; i.e. it seems in fact to be a function not of the isotope mass, but rather of the atomic radius. Indeed, it is well-known that the trend in published deviations from the ideal of $\alpha = 1/2$ tends toward lower values [89]. The absence of an isotope effect in Ru, Os, Zr and Nb_3Sn raises questions about the origin of the attractive interaction responsible for the formation of *Cooper pairs* in these as well as perhaps in metals and compounds.

PHYSICAL FEATURE OF OCCURRENCE AND TRANSPORT MECHANISM FOR SUPERELECTRONS

Potential Eenergy in Shrunken Atoms

Since the itinerant electrons which are derived from the inner filled orbits have not the coherent nature of the electron-pair wave superelectrons at temperatures above T_c, we must consider a mechanism for conserving pre-existing pairs of electrons at the temperature below T_c. The decrease in phonon frequency can be estimated with the increasing of atomic shrinkage ratio in shrunken atoms, so the interaction alone between electron and ion is considered as the attractive mediation for producing electron pairs which compose of time-reversed pairs of quasi-particle. In this case, we must explain why the electrons should attract one another when the electrons have like charges and thus should repel one another instead.

The repulsive and attractive contributions to the interaction among electrons and ions in shrunken atom are shown in Fig. 10, together with that for the total potential



Firure 10. The repulsive and attractive contributions to the interaction among electrons and ions in shrunken atoms T> T_c (left), T< T_c (right)

energy V_{el-el} + V_{el-ion}. The repulsive force gives rise to a positive potential energy, V_{el-el}, between two electrons, and the attractive force does a negative potential energy, V_{el-ion}, between electron and ion. Although electrons' overlaping strengthen a repulsive contribution of V_{el-el}, existence of large number of oxygen probably makes the V_{el-el} lessen, as can be assumed from the relation $T_c = 0.268 * e^{1.31\tau}$ in the previous section, where τ = (Valence Electron Concentration of anions) / (Valence Electron Concentration of cations). For this reason, a screen effect in shrunken atom should be considered. The electron gas is deformed by the combined influences of the electrostatic potential of the positive charge distribution and the induced electrostatic potential of the deformation of the electron gas itself.

With decreasing of atomic radius, the screening effect due to the condensed electron will exert to the V_{el-el} and the Coulomb field will be replaced by one derived from the potential energy [90,91]

$$-\frac{Ze^2}{\varepsilon r}\exp^{-qr} \quad , \tag{5}$$

where ε is a static electric coefficient, Z is the number of electron and q is a screening constant given in the Thomas-Fermi approximation [92,93] [4] by

$$q^2 = \frac{4me^2n^{1/3}}{\varepsilon\hbar^2} \quad , \tag{6}$$

The equation (6) is valid for electrostatic potentials that vary slowly in comparison with the wavelength of an electron. For a more complete theory of screening, we must use a quantumn mechanical perturbation theory which calculates the distortion of the electron states, using a dielectric function, $\mathcal{E}(K)$ [5] (without attention to the charge transfer excitonic effects) by Lindhard [94].

$$\mathcal{E}(K) = 1 + \frac{2me^2k_F}{\pi\hbar^2K^2}\left(\frac{4k_F{}^2 - K^2}{4k_FK}\ln\left|\frac{2k_F + K}{2k_F - K}\right| + 1\right) , \tag{7}$$

K is the wave vector and k_F is Fermi wave number. Since an equation (7) shows a logarithmic singularity with an infinite negative slope at $K = 2k_F$, the potential for $K < 2k_F$ can scatter an electron to a final state of the same energy, enhancing the screening.

Thus by (6), it is clear that the screening effect increases as the density n(r) of electron near Fermi level increases, that is, the atomic shrinkage ratio in shrunken atoms increase due to to Pauli's exclusion principle, as can be seen from interalattice strain analysis in the previous paper and the high pressure effect on Fermi surface and the electronic transition [95]. Consequently, the total potential at the equilibrium radius, r*, in shrunken atoms would be somewhat positive ($|V_{el\text{-}ion}| < |V_{el\text{-}el}|$) when $T > T_C$ (Fig. 10(a)), and the state will be metallic.

Next we consider the electron-ion interaction when $T < T_C$. Judging from a relatively small carrier (of free electron) density ~ $10^{21}/\mathrm{cm}^3$ [68,69], the plasma edge in the far-infrared region [96] and the black color in cuprate oxide superconductors, the number of free electron seem to make decrease, because the free electrons of the normal good conductor screen an optical (electro-magnetic) field and prevent from penetration of photon into the conductor.

---

[4] This approximation is probably valid for shrunken atoms that the amplitude of the electrostatic potential is close to zero.

[5] Strictly speaking, the dielectric function $\mathcal{E}(K,\omega)$ strongly depends on frequency ω, and wavevector K. However, $\mathcal{E}(K,0)$, in one limit, is not treated in this study due to negligible low frequency in shrunken atoms.

The extremely large diamagnetic susceptibility in the superconducting state compared with normal-conducting state also suggests neutralization of screening effects, by the inner closed shells, of the free electrons or outer electrons of s and p orbits in shrunken atoms. These outer electrons and their electrical properties are also constrained by the positively charged nucleus, as well as the inner closed shell electrons. Therefore, we can visualize a physical picture of the condensed electron in shrunken atoms due to increase of an *effective possitive charge effect* and the resulting neutralization of the screening.

When T arrives at T_c, the effective positive charge effect which very tightly binds inner electrons to the nucleus suddenly begin to exert it's influence to all the electrons due to the presents of *electrostatic field fluctuation*, and the screening of the inner closed shell is neutralized. The fluctuation is conected with an electronic polarizability which arises from the displacement of the electron shell relative to the nucleus. It is known that the dielectric constant of atoms at optical frequencies comes almost entirely from this polarizability [97]. Consequently, the positive potential energy V_{el-el} between outer and inner electrons will be lessen at temperature below T_c and the total net potential among electrons and ions will be attractive ($|V_{el-ion}| > |V_{el-el}|$) (Fig. 10(b)). If the fluctuation occurs in the region K $< 2k_F$ when T = T_c , the energy of the inner closed shell electrons will further decrease due to the screening effect by an equation (7), because of extreme enhancement of the interaction between the inner closed electrons and the nucleus. In other words, a drastic decrease of the very strong repulsive interaction among outer and inner electrons and a considerably increase of attractive interaction between the inner closed electrons and the nucleous halt the break-up of the pre-existing pairs of electrons with antiparallel spins in the inner shells. This strong attractive interaction conserves the "spin paired" electrons and is responsible for transition to a superconducting state.

All the even-mass-number orbital electrons derived from the inner closed shells are bosons which are particles with zero momentum and zero spin, and the same orbital can be occupied by any number of bosons [98]. The electron-ion interaction in shrunken atoms leads to a boson ground state seperated from fermion ground state which is derived from free or outer electrons (a *Fermi liquid*) with half-integral spin, by an energy gap 2Δ. Bosons in the ground state are "condensed" in the sense of *Boson-Einstein condensation* and the whole electron system acts as if it were a single entity of ordered state in analogy with liquid helium. It is well known that superconductivity is intrinsically characterized by a macroscopic coherence phase. Thus, the relation between the latter's energy E_g and the former's one E_g' can be presented as the form:

$$E_g' = E_g * e^{-2\Delta(T)/k_BT} , \quad (8)$$

where k_B is Boltzmann constant.

As a result, with decreasing of temperature, it would be expected that both full and empty bands for superconducting conduction would overlap below T_c leading to superconducting state and the number of superelectron will increase uniformly, in analogy with the Mott transition [90] from insulator to metals, which estimates a discontinuous increase in the number of free electrons under the screened Coulomb interaction. Therefore, it seems that the more the radii of cations shrink and temperature decreases, the more the screening and the effective charge effects increase and then the more T_c should increase.

Transport Mechanism

It is considered that the transport mechanism of electrons under direct electron-electron interactions is completely different from others because of the strong electrostatic potential of the ion cores. Indeed, since, for inner or core electrons, the overlap of wavefunctions centered on neighboring atoms is considerably small and the effective mass is large, the electron tunnels slowly one ion to an adjacent ion in the lattice [99]. Then we consider the transport mechanism using the quantum mechanical tunnel effect. The effect had also used to explain the theory of α decay in nuclear physics [100,101] which α particles was able to escape from the large electrostatic potential barrier even though it never had enough energy to surmount it.

In the previous section, it has suggested that continuous shrunken cations as well as chains of Cu-O in the basal plane of the cuprate oxides with high T_c play an active role in the origin of superconductivity, although all ideas that have been proposed up till now merely emphasize the importance of two-dimensional layers of copper and oxygen. Superconductivity due to cation-cation chains has been overlooked. Hence, we can visualize four combinations of two contributions for superconductivity; (1) chain of Cu-O alone is predominant, (2) main effect of Cu-O chains and subordinate existence of cations, (3) continuous shrunken cations alone are predominant and (4) main effect of cation chains and subordinate effect of Cu-O chains. However, both items of (1) and (3) may be negligible from the results of the previous sectionr.

Transport in Cu-O Chains : Figure 11 shows a relation between T_c and the cation

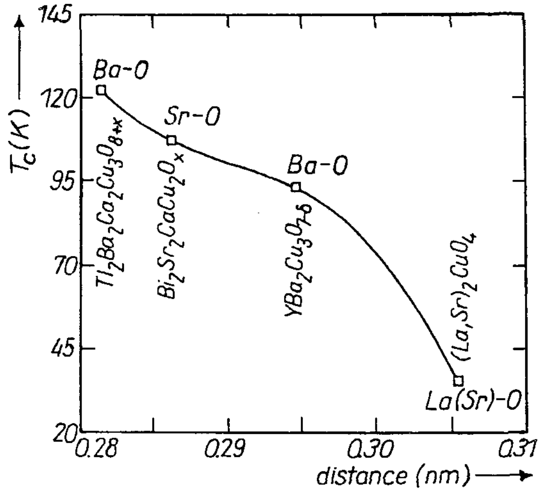


Figure 11. The relation between and the cation (with 9-coordination above the perovskite layer)-oxygen (in Cu-O chains on the based plane) distances of four cuprate oxides, $(La,Sr)_2CuO_4$, $YBa_2Cu_3O_{7-\delta}$, $Bi_2Sr_2CaCu_2O_x$ and $Ti_2Ca_2Ba_2Cu_3O_{8+x}$

(with 9-coordination above the perovskite layer) - oxygen (in Cu-O chains on the basal plane) distance of four cuprate oxides analyzed in the previous paper, where a decrease of the distance contributes to increase in T_C. Therefore, we consider the superconductivity along the Cu-O chains using $Bi_2Sr_2CaCu_2O_x$ as an example. The physical feature is depicted in Fig. 12(a) and (b), which presents schematically

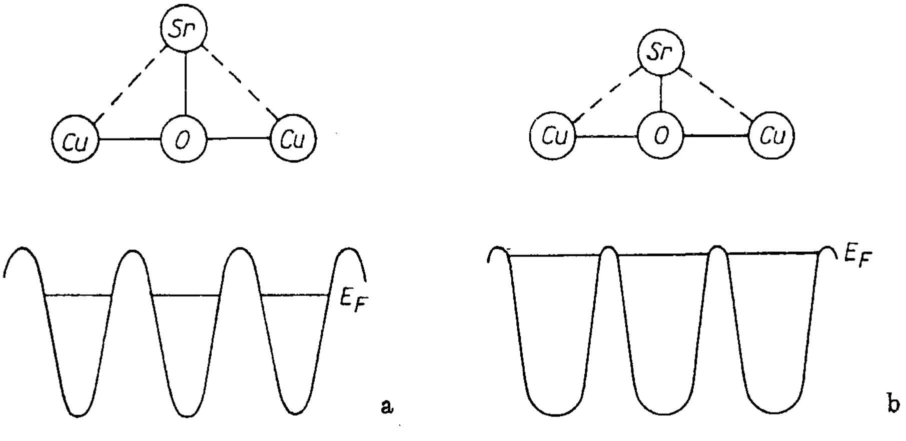


Figure 12. Variation of potential energy of a conduction electron pair in the field of the inner filled copper and oxygen shells of a linear periodic well (a) in non-shrunken atoms and (b) in shrunken atoms

the periodic potential wells of the inner filled copper and oxygen shells. Since shrunken Sr cations atom are forced to draw to the oxygen atom, the electrostatic energy of the system changes; each well width widdens and the barrier width between copper and oxygen becomes narrower It is generally known that ground orbital energy for the electrons in a periodic square well potential is lowered as the wells come closer together [102].

In analogy with Josephson tunneling effect (weak superconductivity) [103,104] which is a tunneling of coupled electron pairs with the charge of *2e* and the mass of *2m* without any accompaning voltage drop, one may think of the paired electrons as transporting through *a virtual tunnel* in the one-dimentional barrier shown in Fig. 12 (b). Here, we consider the combination of the four copper *d*-electron states passing through an oxygen one. The phase of *d*-state wave functions are defined in Fig. 13, where Cu singlet electron pairs derived from 3*d* orbitals is formed between two copper atoms. This means that exchange of superconducting pairs can occur because there is an overlap of the electron-pair wave functions in the two copper atoms.

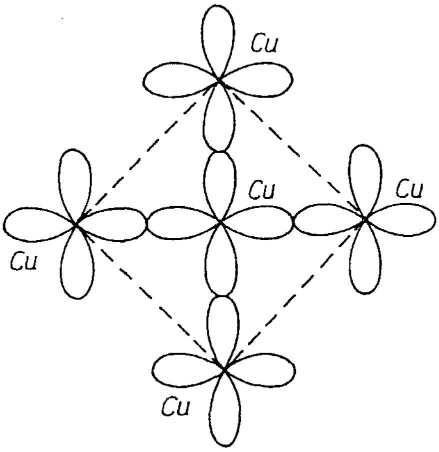


Figure 13. Schematic diagram of the superelectron transport between *d*-state wave functions of copper passing through the *p* state of oxygen in the Cu-O series

The Cu-O single band models based on hole carrier mechanism are proposed by Imada [105] and Zhang *et al* [106]. However, both models are intrinsically different from an above mentioned model under strong electron correlation. The former is emphasized that mutually attractive interaction of singlet pairs formed by oxygen and neighboring copper holes leads to superconductivity. The latter is based on the hybridization bands of which a local singlet moves through the lattice of Cu $^{2+}$ ions as a hole in the single-band effective Hamiltonian of the strongly interacting Hubbard model.

Thus, the electrons can transfer to a nearest neighbor copper well (≈ 0.37 nm [9]) by the charge-, mass- and phase coherence-tunneling when there is a non zero voltage across the barrier between copper atoms [107]. Both electrons are derived from a completed 3*d*-electron shell, so both total orbital angular magnetic moment,*l*, and total spin angular moments,*s* of the paired electrons are zero.

Transport in Sr Atoms : Since shrunken Sr atoms are continuously connected with Sr one in the next neighbor unit cell, the charge tunneling transport between Sr atoms easily takes place compared with that of Cu-O chains. The mean free path of the superelectron pairs is just an interatomic spacing (≈ 0.38 nm [9]). The derivation of the pairs will be 3*d* inner orbit , taking the energy level of inner electrons into consideration, because *s* and *p* electrons which are most outer ones are used to form the lattice skeleton modified by the strong bonds associated with the affinity of I-III group elements for oxygen, as described in early paper [10]. Since Sr has also a closed 3d-electron shell, both *s* and *l* of the d orbit electrons are zero. Although the coherence length for the cation in cuprate oxide superconductors has not reported yet, a necessary, but not sufficient, condition for producing the superconducting ground state can be considered that the radii of available orbitals are large. For this reason, cation with large ionic radius is desirable for the occurrence of superconductivity, as pointed out by the previous section. Indeed, all the atomic radii of cation elememts such as Ba, Sr and Ca which constitute superconducting oxides, are about 0.17 nm [57] except for Cu. Copper alone seems to form as small chains of Cu-O in superconductivity, as mentioned above.

Moreover, heavy-electron superconductors [108] also consist of rare earth and actinide elements with large atomic radii. In these cases, it is not clear at present whether the dominant transport electrons are *p*-triplet or BCS-singlet paired ones although it has been argued that the electrons with triplet spin pairing are responsible for heavy-electron superconductivity. Superconductivity also may be related to paired electrons derived from completely filled inner shells such as the 4*f* and 5*d* levels [9]. Therefore the compounds and alloys of rare earth and actinide elements with large radii are candidates for high T_c superconductors. In addition, it is known that the 4*f* and 5*d* electronic levels are very close and the actual state which the atom assumes is very sensitive to the density and pressure [109].

HAMILTONIAN

We consider a conduction electron pair in condensed electron state of shrunken atom in momentum or *k* -space. The treatment of the motion of the electrons is an example of a many-body problem in a strict sense of the word. Here, we may be thought that the Hamiltonian is the sum of five terms corresponding to the electrons, the ion, interaction between them, the paired electrons tunneling and external field:

$$H = H_{el} + H_{ion} + H_{el\text{-}ion} + H_T + H_{ex} \ . \qquad (9)$$

The first term, H_{el} is the Hamiltonian of the electrons which includes interactions among electrons. We assume that each electrons moves in the periodic field of atom. Then

$$H_{el} = \sum_k \frac{p_k^2}{2m} + \frac{1}{8\pi\varepsilon} \sum_{k,k'} \frac{e^2}{|r_k - r_{k'}|^2} \qquad k = 1,2,\cdots n, \qquad (10)$$

and r_k repsents the coordinates of the *k* th electron. The wave function of H_{el} are the Bloch functions Ψ_k with energy E_k :

$$H_{el}\Psi_k = E_k\Psi_k \ . \qquad (11)$$

Strictly speaking, one might say that the superelectrons can be represented together by a many-electron wave function Ψ_G which is a product of pair wave functions [110]:

$$\Psi_G\ (r_1,r_2, \ldots, r_n) = \Phi(r_1,r_2)\Phi(r_3,r_4) \ldots \Phi(r_{n-1},r_n), \qquad (12)$$

where n/2 is the total number of pairs, r_n stands for the position coordinates (x_n, y_n,z_n) of the *n* th electron, and Φ's on the right hand side are the same for all pairs. The pair may be regarded as a particle obeying Bose-Einstein statistics.
The Hamiltonian for the ion, H_{ion} can be expressed in the form:

$$H_{ion} = \sum_i \frac{p_i^2}{2m} + \frac{1}{2} \sum_{i,i'} V_{ion}\,(R_i - R_{i'}) \qquad i = 1,2,\cdots\ n',\ i' = 1,2,\cdots\ n', \qquad (13)$$

and R_j represents the coordinates of the *i*th ion. The term of interaction between electron and ion are linear in the displacements of the nuclear coordinates from their equilibrium positions R_i, and it is presented as the form:

$$H_{el\text{-}ion} = \sum_{k,i} V_{el\text{-}ion}(r_k - R_i) \qquad k = 1,2, \ldots\ n,\ i = 1,2, \ldots\ n'. \qquad (14)$$

Strictly, $H_{ion\text{-}ion} = H_{ion\text{-}ion} + H_{ph}$, and $H_{el\text{-}ion} = H_{el\text{-}ion} + H_{el\text{-}ph}$, where H_{ph} is the Hamiltonian for the phonon. We shall neglect phonon effects, as described above.

Here we describe the weak coupling between the two superelectrons with the spin-conserving tunneling Haniltonian H_T. The Haniltonian was first introduced by Cohen *et al* [111], for the tunneling process from normal metal to superconductor, and then extended by Paris and coworkers [112] for two superconductors separated by a barrier. We further expand it to the form in view of the paired electrons:

$$H_T = \sum_{ll'\sigma} (T_{ll'} a^+_{l\sigma} a_{l\sigma} + T^*_{ll'} a_{l\sigma}{}^+ a_{l\sigma}), \qquad (15)$$

where $a_{l\sigma}{}^+$ and $a_{l'\sigma}$ are creation and destruction operators and the wave vector l or l' belong to the superelectrons from one atom to the neighbor, respectively, and σ is spin quantum index. T^* presents time-reversal symmetry for H_T in the tunneling matrix element T_{ll}.

The Hamiltonian for external field, H_{ex} can also set equal to zero.

Since the effective interactions between a pair of ion and between electron and ion will be screened as a result of the variation of positive charge density which surrounds any ion and electron, respectively, we must include the screening effect in the equations (13) and (14).

Thus by (13) we have

$$H_{ion} \approx \sum_i \frac{p_i^2}{2m_i} + \frac{1}{2} \sum_{i,i'} \frac{(Ze)^2}{\varepsilon |R_i - R_{i'}|} \exp^{-q|R_i - R_{i'}|} , \qquad (16)$$

and by (14)

$$H_{el\text{-}ion} \approx \sum_{ki} \frac{-Ze^2}{\varepsilon |r_i - R_j|} \exp^{-q|r_k - R_i|} \qquad (17)$$

WAVE FUNCTION FOR SUPERELECTRONS

Since the motion of superelectron which belongs to the inner closed shells reflects the strong electrostatic potential of the ion cores, both a pseudo-potential and a plane wave function are not always appropriate for description of the conduction mechanism of the superelectrons. The pseudo-potential theory does not treat the kinetic and potential energy near the nucleus, and energitically seperates conduction electrons and shell electrons. The plane wave theory treats the conduction of outer orbital electron as one or two plane waves alone under a weak pertubation of an interaction between an electron and an element's lattice.

Indeed, recently, many phenomena which cannot be explained by the band theory have reported for the cuparate oxide superconductors [113,114]. Thus, it is presentaly considered that there is not a suitable description of the conduction of the superelectrons. Therefore, the conduction mechanism must call for a new concept, taking into account for both the electrostatic potential and interaction between the element's lattice and it's electron in the inner ion cores. Then we will describe the transport of superelectron using *virtual tunneling*.

Transport in Cu-O Chains

The following physical conditions are estimated in the condensed electron state: (1) The superelectrons are derived from $d_{x^2-y^2}$ inner orbits of Cu. The electrons are a kind of itinerant ones. (2) The electrons are correlated each other and form a bound pair within the half interatomic region. (3) This electron pair is intrinsically different from *Cooper pairs* . (4) The driving force of the conduction is an electrostatic attraction between electrons and ion cores under ultra-high pressure effect due to Pauli's exclusion principle in shrunken atoms. (5) And consequently, the conduction direction is along the shrunken bond one. (6) Phonon effect for motion of the electrons is negligible. (7) The heat transport by the motion in the electron is also negligible. (8) The conduction of the paired electrons is not by the thermally activated hopping mechanism which an electron jumps from one localized state to another in semiconductor at low temperature [115,116].

Here we consider transport of coupled electron pairs as one body problem. As suggested in phonon effect of the previous section, supercurrent is not subjected to scatter by thermal vibration of lattice. And scattering of the electron pairs in the superconductors is indeed not inhibited by presence of the energy gap 2Δ in eq. (8) and there is no resistance [6]). So, in periodic well in Fig. 12 (b), we can consider that the electron pairs can go over from the inner closed shells to the nearest neighbor one by tunneling. This problem is treated using Kroning-Penney model [117].

Assumed the paired electrons of energy E in one well whose width is a, moves from left to right to strike a barrier whose height is Vo and whose thickness is b. When $Vo > E$, a set of solutions to Schrodinger's equation

$$\frac{d^2\Psi_G}{dx^2} + \frac{2m}{\hbar}(E-Vo)\Psi_G = 0 \ , \tag{18}$$

in zones I and II is

$$\Psi_{GI} = A\,e^{iKx} + B\,e^{-iKx} \qquad 0 < x < a, \tag{19}$$

$$\Psi_{GII} = C\,e^{Qx} + D\,e^{-Qx} \qquad -b < x < 0, \tag{20}$$

with

$$K = \frac{(2m^*E)^{1/2}}{\hbar} = \frac{p}{\hbar} = \frac{1}{\lambda} \ , \tag{21}$$

$$Q = \frac{(2m^*|E-Vo|)^{1/2}}{\hbar} \ , \tag{22}$$

$$\Psi_G\,(a<x<a+b) = \Psi_G\,(-b<x<0)e^{ik(a+b)} \ , \tag{23}$$

where p is the momentum and λ the *de Broghie* wavelength, m* is the effective mass of the paired electrons. It is known that the inertial masses increase extremely when the overlap of wave function of the electrons on neighboring ions is weak [118]. Applying the continuity conditions on the wave function and its first derivatives at x=0 and x=a, we can finaly obtain a solution,

$$[(Q^2-K^2)/2QK]\sinh Qb \sin Ka + \cosh Qb \cos Ka = \cos k(a+b) \ . \tag{24}$$

The superconducting state is constructed by making suitable linear combinations of single-electron wave functions which inhibit variations of the order

---

[6] Strictly speaking, it is believed that in "gapless" superconductors scattering of pairs is inhibited not by the presence of an energy gap but by the strongly correlated nature of the pair wave function.

parameter over distances less than the coherence length ξ [119,120] Several groups have estimated the lengths from critical magnetic field and fluctuation conductivity data [121,122]. The smallest values in inter-planar ($\xi_{\perp}$ ~0.36 nm [123]) are in good agreement with the mean free path of the superelectron pairs. Therefore, this short-range ordered pairing distance ξ can be considered as the fundamental size of the coupled electron pairs in cuprate oxide superconductors and the spatial extent of the pair wave function given by (12).

Transport In Sr Atoms

The physical conditions of this transport is same as those in Cu-O chains expect for the derivation and the mean free path of superelectrons. The electrons will be derived from 3*d* inner closed orbit, and their mass *will be different* from ones in Cu-O chains. The path will be just an interatomic spacing. However, the conduction of the paired electrons can be treated by the same formulae (16)-(22) above mentined. In the virtual tunneling model mentioned above, one can easily envisage a *perfect conductor* as a solid in which electrons occupy Bloch states with zero scattering, rather than a superconductor as a solid with infinite D.C. conductivity (~10^{23} ohm^{-1} cm^{-1} [124]).

SPIN STATE OF THE SUPERELECTRON PAIRS

Pair states more general than the single pair are possible - in the heavy-Fermion-liquid superconductors [108,125], for examples, the pairs are in spin-triplet state which have both spin and orbital momenta (*p*-type pairing). One "obvious" *experiment* to do is Josephson tunneling using a known *s*-paired superconductor as the other electrode. It has been argued that by symmetry no pair current should exist, because the wave function of a pair in the spin-singlet state is symmetric in the space part and antisymmetric in the spin part for the interchange of the two electrons [126]. Indeed, experimental results for the Josephson effect have to put severe constrains on the possibility of the *p*-type pairing [127,128].

However, it is not clear at present whether the condensation of electron pairs is *s*-type singlet pairing such as *Cooper pairs* or even-parity anisotropic pairing. The latter pairing mechanism mediated by spin fluctuations near an spin-density-wave (SDW) instability has reported in the heavy-fermion superconductors such as UPt_3 [129,130], $CePb_3$ [131], or in some compounds under pressure such as the Bechgaard ditetramethyltetraselenaful -valence salts $(TMTSF)_2X$ ($X=PF_6$, AsF_6, ClO_4, $\cdots$) [5]. In this study, it will be probably the latter, taking relaxation of the strong Coulomb repulsion in the condensed electron state of shrunken atom into consideration. One possibility is to assume that the superconductivity in the cuprate oxide superconductors is of singlet *d* wave-like pairing than of singlet *Cooper pairs* type. Moreover, it is considered that the superconducting state in the cuprate oxide should be clasified as having odd or even parity, rather than singlet or triplet character, taking rotational symmetry in spin space into account.

In this study, the locally strong correlation among electrons in shrunken atoms could sucessfully explain in three dimensional Cartesian coordinates, using attractive mediation of ion under a screened Coulomb interaction. Itinerancy of superelectrons derived from the inner *d* closed shells of Cu and Sr atoms could also well modelled in momentum space, using *virtual tunneling*, but seemd physically intutive. We can not explain why certain substances suddenly become superconductivity at a specific temperature. Further work in this interesting area is called for.

REFERENCES

1. C.W.Chu and L.R.Testardi,Direct observation of enhanced lattice stability in V_3Si under hydrostatic pressure,Phys.Rev.Lett.,1974,**32**,766-69.
2. R.N.Sheltron and D.C.Johnston,Pressure dependencies of the superconducting and magnetic critical temperatures of ternary rhodium borides, High Pressure and Low TemperaturePhysics, eds.C.W.Chuand, J.A.Woollam, Plenum, New York, 1978,p.p.409-17 .
3. C.W.Chu, P.H.Hor, R.L.Meng, L.Gao, Z.J.Huang and Y.Q.Wang, Evidence for superconductivity above 40 K in the La-Ba-Cu-O compound system, Phys. Rev. Lett., 1987, **58**, 405-07.
4. P.H.Hor,L.Gao,R.L.Meng,Z.L.Huang,Y.Q.Wang,K.Forster,J.Vasslious,C.W.Chu, M.K.Wu, J.Ashburn and C.J.Torng, High-pressure study of the new Y-Ba-Cu-O superconducting compoud system,Phys.Rev.Lett.,1987,**58**,911-12 .
5. K.Yamaji, Theory of field-induced spin-density-wave in bechgaard salts, Synthetic Met.,1986,**13**, 29-43.
6. H.Takeya,H.Takei,Y.Koike,T.Fukase,T.Shishida,N.Toyota and Y.Syono,Shock-loading effects on superconducting and ferromagnetic transitions of $ErRh_4B_4$, J.Jpn. Appl.Phys., 1986, **25**,1954-55.
7. R.J.Cava, B.Batlog, C.H.Chen, E.A.Chen, E.A.Rietman, S.M.Zahurak and D.Werker, Single-phase 60-K bulk superconductor in annealed $Ba_2YCu_3O_{7-\delta}$ $(0.3<\delta<0.4)$ with correlated oxygen vacancies in the Cu-O chains,Phys.Rev. 1987,**B36**,5719-22 .
8. M.Fukuhara,A.S.Bhalla,L.N.Mulay, and R.E.Newnham,Aurivillius-Popper mixed superconductors in BiO-CuO-$(Sr_{0.5},Ca_{0.5})O$ system,J.Mater.Research,1989, **4**,273-82 .
9. M.Fukuhara and H.A.Mckinstry,Intralattice strain analysis in superconducting crystals and superconducting elements, Phys.Stat.Sol.(b),1990,**157**,357-77.

10. M.Fukuhara,A.S.Bhalla,R.E.Newnham,L.E.Cross and R.Roy, Superconductors in BiO-CuO-($Sr_{0.5}$,$Ca_{0.5}$)O system,Mater.Lett.1988,**6** (11,12)398-400 .

11. J.G.Bednorz and K.A.Muller,Possible high Tc superconductivity in the Ba-La-Cu-O system,Z.Phys.1986,**B64**,189-93;J.G.Bednorz,M.Takashige,K.A.Muller, Susceptibility measurements support high Tc superconductivity in the Ba-La-Cu-O system.Europhys.Lett.,1987,**3**,379-84 .

12. M.K.Wu,J.R.Ashuburn,C.J.Torng,P.H.Hor,R.L.Meng,L.Gao,Z.J.Huang,Y.Q. Wang and C.W.Chu,Superconductivity at 93 K in a new mixed-phase Y-Ba-Cu-O compound system at ambient pressure, Phys.Rev.Lett.1987, **58**, 908-10; S.Hikami,T.Hirai and S.Kagoshima,Jpn.J.Appl.Phys.,1987,**26**(4)L314.

13. H.Maeda,Y.Tanaka,M.Fukutomi and T.Asano, A new high Tc oxide superconductor without rare earth element, J.J.Appl.Phys. Lett,1988 , **27**(2), L209-11; M.A.Subramanian,C.C.Toratdi, J.C.Calabrese, J.Gopolakishnan,K.J.Morrissey, T.R.Askew,R.B.Flippen,U.Chavdhry and A.W.Sleight,A new high-temperature superconductor:$Bi_2Sr_{3-x}Ca_xCu_2O_{8+y}$,Science,1988,**239** (Feb.26)1015-17.

14. Z.Z.Sheng,A.M.Herman,A.ElAli,C.Almasan,J.Estrada,T.Datta and R.J. Matson, Superconductivity at 90 K in the Tl-Ba-Cu-O system,Phys.Rev. Lett.1988,**60** (10)937-40 ; C.C.Torardi,M.A.Subramanian, J.C.Calabrese,J.Gopalakrishnan, K.J.Morrissey, T.R.Askew, R.B.Flippen,U.Chowdhry and A.W.Sleight,Crystal structure of $Tl_2Ba_2Ca_2Cu_3O_{10}$, a 125 K superconductor,Science, 1988, **240**, 631-34.

15. N.Nucker,J.Fink,J.C.Fuggle,P.J.Durham and W.M.Temmerman,Evidence for holes on oxygen sites in the high Tc superconductors $La_{2-x}Sr_xCuO_4$ and YBa_2 CuO_{7-y}, Phys.Rev.1987, **B37**(10) 5158-63; Y.Gao, T.J.Wagner, D.M.Hill, H.M. Meyer III,J.H.Weber, A.J.Arko,B.K.Flandermeyer and D.W.Capone II, Chemistry of High-Temperature Superconductors, ed.,D.C.Nelson et al., American Chemical Society,Washington D.C., 1987,p.p.212-25.

16. K.Kumagai, Y.Nakamichi, I.Watanabe, Y.Nakamura, N.Wada and P.Lederer, Linear temperature term of heat capacity in insulating and superconducting La-Ba-Cu-O system,Phys.Rev.Lett.1988, **60**(8)724-27.

17. K.Kitazawa, T.Atake, M.Sakai, S.Uchida, H.Takagi, K.Kishio, H.Hasegawa, K.Fueki, Y.Saito and S.Tanaka, Specific heat and superconductivity of $(La_{0.925}Sr_{0.075})_2CuO_4$,Jpn.J.Appl.Phys.,1987,**26**(5)L751-53; Z.G.Khim,S.C. Lee,B.J.Suh,Y.W.Park,I.S.Yu and J.C.Park,Superconductivity in single-phase $Y_1Ba_2Cu_3O_{9-x}$ and thermoelectric power measurement, Phys. Rev., 1987,**B36**(4) 2305-07 .

18. M.Gurvitch and A.T.Fiory, Resistivity of $La_{1.825}Sr_{0.175}CuO_4$ and $YBa_2Cu_3O_7$ to 1100 K: absence of saturation and its implications,Phys.Rev.Lett.,1987, **59**(12)1337-40.

19. J.Bardeen,L.N.Cooper and J.R.Schrieffer,Theory of superconductivity, Phys. Rev. 1957,**108**(5)1175-1204.

20. P.W.Anderson,The resonating valence bond state in La_2CuO_4 and superconductivity,Science,**235**,1196-98 ; P.W.Anderson,G.Basharan, Z.Zou and T.Hsu, Resonating-valence-bond theory of phase transitions and superconductivity in La_2CuO_4-based compounds, Phys.Rev.Lett.,1987,**58**(26), 2790-93.

21. A.E.Ruckenstein,P.J.Hirschfeld and J.Appel,Mean-field theory of high Tc superconductivity: The superexchange mechanism,Phys.Rev., 1987, **B36** (1)

857-60 ; K.Miyake, T.Matsuura, K.Sano and Y.Nagaoka, Electronic structure, spin fluctuation, and superconductivity of excited Hubbard model: A possible mechanism of high Tc in oxide superconductors, Physica,1987,**148B**,381-84.

22. J.R.Shrieffer,X-G.Wen and S.-C,Zhang,Phys., Spin-bag mechanism of high-temperature superconductivity,Phys.Rev.Lett., 1988,**60**(16)944-47.

23. P.W.Anderson,Antiferromagnetism. Theory of superexchange interaction, Phys. Rev.,1950,**79**(2) 350-56; J.Yamashita, Theory of superexchange interaction in MnO crystal,Jpn.J.Phys. Soc.,1954,**9**(3)339-45.

24. D.Vaknin,S.K.Sinha,D.E.Moncton,D.C.Johnston,J.M.Newsam,C.R.Safinya and H.E.King. Jr., Antiferromagnetism in La$_2$CuO$_{4-y}$,Phys. Rev.Lett.,1987,**58** (26)2802-05.

25. A.Khurana,Superconductivity seen above the boiling point of nitrogen,Physcs Today ,1987,April,p.p.17-23.

26. M.Fukuhara, G.W.Smith II,New approach to the theory of high-temperature superconductivity,Phys.Stat.Sol.(b),1989,**156**,583-96.

27. J.P.Glusker and K.N.Trueblood, Crystal Structure Analysis, 2 nd edition, Oxford UniversityPress,NewYork,1985,p.p.166; A.Smith,MolecularEditor,Kinko'Service, Santa Babara,1987, p.p.1.

28. International Tables for X-ray Crystallography, **Vol.III**, Kynoch Press, Birmingham, England,1968,p.p.257.

29. R.D.Shannon and C.T.Prewitt,Effective ionic radii in oxides and fluorides , Acta.Cryst.,1969,**B25**,925-46 .

30. R.Mailfert,B.W.Batterman and J.J.Hanak,Observations related to the order of the low temperature structural transformation in V$_3$Si and Nb$_3$Sn,Phys. Status. Solidi,1969,**32**,K67-69 .

31. J.W.Ekin,Strain scaling law for flux pinning in practical superconductors.Part 1: Basic relation and application to Nb$_3$Sn conductors, Cryogenics, 1980, **20**, 611-24.

32. N.F.Mott,The transition to the metallic state,Phil.Mag.,1961,**6**,287-309; N.F.Mott, Metal - Insulator Transitions, Taylor and Francis, London,1974,p. p. 5.

33. G.Shirane and J.D.Axe,Neutron scattering study of the lattice-dynamical phase transition in Nb$_3$Sn,Phys.Rev.,1971,**B4**,2957-63.

34. J.Patel,B.W.Batterman and E.I.Blount,Search for sublattice distortion in V$_3$Si, Phys.Rev.,1968,**166**,616-21.

35. B.A.Hatt,J.K.R.Page and V.G.Rivlin,The structure and superconducing transitions of some pseudobinary 'β-W' alloys,J.Low-Temp.Phys.,1973,**10**,285-98.

36. M.Francois,K.Yvon,P.Fischer and M.Decroux, Structural phase transition at 150K in the high-temperature superconductor La$_{1.85}$Sr$_{0.15}$CuO$_4$,Solid State Comm.,1987,**63**, 35-40.

37. R.E.Newnham,R.W.Wolfe and J.F.Dorrian,Structural basis of ferroelectricity in the bismuth titanate family,Mat.Res.Bull.,1971,**6**,1029-39 .

38. Y.Hidaka,Y.Enomoto,M.Suzuki,M.Oda and T.Murakami, Anistropic properties of superconducting single-crystal $(La_{1-x}Sr_x)_2CuO_4$,Jpn. J.Appl. Phys.,1987, **26**, L377-79.

39. K.Kishio,K.Kitazawa,N.Sugii,S.Kanbe,K.Fueki,H.Takagi and S.Tanaka, High-Tc superconducting oxides solid solutions $(La_{1-x}(Ba,Sr,Ca)_x)_2CuO_{4-\delta}$, Chem.Lett. ,1987,635-38.

40. T.Fujita, Y.Aoki, Y.Maeno, J.Sakurai, H.Fukuba and H.Fujii, Crystallographic, magnetic, and superconductive transition in $(La_{1-x},Ba_x)_2CuO_{4-y}$,Jpn.Appl. Phys.,1987, **26**, L368-70 .

41. P.H.Grant,S.S.P.Parkin,V.Y.Lee,E.M.Enger,M.L.Ramirez,J.E.Vazquez, G.Lim, R.D.Jacowitz and R.L.Greene,Evidence for superconductivity in La_2CuO_4,Phys.Rev.Lett.,1987,**58**,2482-85; S.M.Fine,M.Greeblatt,S.Simizu and S.A.Friedberg,Effect of nominal composition on superconductivity in La_2CuO_{4-y},Chemistry of High-Temperature Superconductors, ed., D.C.Nelson et al. American Chemical Society, Washington,DC,1987,p.95-101.

42. D.C.Johnston, A.J.Jacobson, J.M.Newsam, J.T.Lewandowski, O.P.Groshorn, D.Xie and W.B.Yelon, Variation in the structural, magnetic, and superconducting properties of $YBa_2Cu_3O_{7-x}$ with oxygen content, Chemistry of High-Temperature Superconductors,ed., D.C.Nelson et al.,American Chemical Society, Washington,DC,1987,P.136-51 .

43. P.M.Horn,D.T.Keane,G.A.Held,J.L.Jordan-Sweet,D.L.Kaiser,F.Holtzberg and T.M.Rice,Orthormbic distortion at the superconducting transition in $YBa_2Cu_3O_7$:Evidence for anistropic pairing, Phys.Rev.Lett.,1987,**59**,2772-75 .

44. T.R.Dinger, T.K.Worthington, W.J.Gallagher and R.L.Sandstrom,Direct observation of electronic anistropy in single-crystal $Y_1Ba_2Cu_3O_{7-x}$, Phys.Rev. Lett., (1987) **58**(25), 2687-90; Y.Hidaka,Y.Enomoto and M.Suzuki, Anistropy of the upper critical magnetic field in single crystal $YBa_2Cu_3O_{7+y}$, Jpn. J.Appl.Phys., 1987,**6**,L726-28.

45. G.C.Vezzoli, Lt.R.Benfer and W.Spurgen, Structural and charge-transfer descrition of high-Tc superconductivity in $Y_1Ba_2Cu_3O_{7-\delta}$, Novel Superconductivity,ed.,S.A.Wolf andV.Z.Kresin,Plenum Press,New York, 1987, P.1017 -28; Y.Maeno,T.Tomita, M.Kyogoku, S.Awaji, Y.Aoki, K.Hoshino, A.Minami and T.Fujita,Substitution for copper in a high-Tc superconductor $YBa_2Cu_3O_{7-\delta}$, Nature,1987,**328**,512-14.

46. J.D.Jorgensen,H.B.Schuttler,D.G.Hinks,D.W.Capone,II,K.Zhang,M.B. Brodsky and D.J.Scalapino,Lattice instability and high-Tc superconductivity in $La_{2-x}Ba_xCuO_4$,Phys.Rev.Lett.,1987,**58**,1024-27.

47. L.C.Bourne, A.Zettl, T.W.Barbee,III and M.L.Cohen, Complete absence of isotope effect in $YBa_2Cu_3O_7$: Consequences for phonon-mediated superconductivity, Phys.Rev. ,1987,**B36**, 3990-93.

48. R.J.Cava, B.Batlogg, C.H.Chen, E.A.Rietman, S.M.Zaharak and D.Werder, Single-phone 60 K bulk superconductor in annealed $Ba_2YCu_3O_{7-\delta}(0.3<\delta<0.4)$ with correlated oxygen vacancies in the Cu-O chains,Phys.Rev.,1987,**B36**, 5719-22.

49. J.M.Tarascon, Y.LePage, W.R.Mckinnon,G.W.Hull, M.Giround and D.M.Hwang, Crystal substructure and physical properties of the superconducting phase $Bi_4(Sr,Ca)_6Cu_4O_{16+x}$,Phys.Rev.,1988,**B37**,9382-89.

50. S.Nomura,T.Yamashita,H.Yoshino and K.Ando,Single-crystal growth of $Bi_2(Sr,Ca)_{3-d}Cu_2)_x$ and its superconductivity,Jpn.J.Appl.Phys.,1988,**27**,L1251-53 .

51. E.Takayama-Muromachi, Y.Uchida, A.Ono, F.Izumi, M.Onoda, Y.Matsui, K. Kosuda,S.Takeyama and K.Kato, Identification of the superconducting phase in the Bi-Ca-Sr-Cu-O System,Jpn.J.Appl.Phys., 1988,**27**,L365-68.

52. F.Beech,S.Miraglia,S.Sanforo and R.S.Roth,Neutron study of the crystal structure and vacancy distribution in the superconductor $Ba_2YCu_3O_{9-\delta}$, Phys. Rev., 1987,**B35**,8778-81.

53. W.B.White,F.Dachille and R.Roy,High-pressure-high-temperature polymorphism of the oxides of lead,J.Am.Cer.Soc.,1961,**44**,170-74.

54. N.R.Serebrynaya,S.S.Kobalkina and L.F.Vereschagin,Crystal structure of tin oxide at high pressure,Soviet Phys. Doklady,1970,**14**,672-74.

55. A.M.Herman,Z.Z.Sheng,D.C.Vier,S.Schltz and S.B.Oseroff,Magnetization of the 120-K Ti-Ca-Ba-Cu-O superconductor,Phys.Rev. ,1988,**B37**, 9742-44.

56. C.C.Torardi,M.A.Subramanian,J.C.Calabrese,J.Gopalakrishnan,K.J.Morrissey, T.R.Askew, R.B.Flippen, U.Chowdhry and A.W.Sleight, Crystal structure of $Tl_2Ba_2Ca_2Cu_3O_{10}$, a 125 K superconductor,Science, 1988, **240**,631-34.

57. P.Schwarzkopf and R.Kieffer,Refractory Hard Metals,Mackmillan,New York,1953, p.p.29.

58. A.W.Sleight,Chemistry of high-temperature superconductors, Science, 1988, **242**,1519-27; J.Gopalakrishnan,M.A.Subramanian and A.W.Sleight,Superconducting and nonsuperconducting analogs of $Bi_2Sr_2CaCu_2O_8$: The role of electronegativity,J.Solid State Chem.,1989,**80**,156-60.

59. H.Bilz, Uber elektronenzustande von hartstoffen mit natriumchloridstruktur, Z.Phys.1958,**153**,338-58.

60. M.Fukuhara,T.Mitsuda,Y.Katsumura and A.Fukawa,Sinterability and properties of $Ti(N_{1-x},O_x)_y$-(V,Ta)C-Ni sintered alloys having a golden colour,J.Mater.Sci., 1985,**20**,710-17.

61. H.R.Khan, C.J.Raub, W.E.Gardner, W.A.Fertig, D.C.Johnston and M.B.Maple, Magnetic and superconducting properties of niobium oxides, Mat. Res. Bull., 1974,**9**,1129-35.

62. N.J.Doyle, J.K.Hulm,C.K.Jones,R.C.Miller and A.Taylor, Vacancies and superconductivity in titanium monoxide,Phys.Lett. ,1968,**26A** ,604-06.

63. R.W.McCallum, D.C.Johnston, C.A.Luengo and M.B.Maple, Superconducting and normal state properties of $Li_{1+x}Ti_{2-x}O_4$ spinel compounds. II. low-temperature heat capacity,J.Low Temp. Phys. 1976,**5**,177-93 .

64. A.W.Sleight, J.L.Gillson and P.E.Bierstedt, High-temperature superconductivity in the $BaPb_{1-x}Bi_xO_3$ system,Solid State Comm. ,1975,**17**,27-28.

65. M.G.Bowler,Nuclear Physics, Pergamon Press,Oxford,1973,p.p.15.

66. T.D.Clark,Superconductivity,Solid State Science,ed.,D.L.Weaire and C.G. Windsor, Adam Hilger, Bristol,1987, p.p.169.

67. T.Ekino and J.Akimitsu,Superconducting tunneling inY-Ba-Cu-O system, Jpn. J. Appl. Phys.,1987,**26**,L452-53 ; I.Iguchi, H.Watanabe, Y.Kasai, T.Mochiku,

A.Sugishita and E.Yamaka, Tunneling spectroscopy of Y-Ba-Cu-O compound, Jpn. J.Appl.Phys., 1987,**26**,L645-46.

68. D.M.Eagles,Superconductivity at very low carrier concentrations and indications of a charged bose gas in $SrTi_{0.97}Zr_{0.03}O_3$,Solid State Comm.,1986,**60**, 521-24 ; Z.Z.Wang,J.Clayhold, N.P.Ong, J.M.Tarascon, L.H.Greene, W.R. Mckinnon and G.W.Hull,Variation of superconductivity with carrier concentration in oxygen-doped $YBa_2Cu_3O_{7-y}$, Phys.Rev.,1987,**B36**(13)7222-25.

69. M.Suzuki and T.Murakami, Hall effect in superconducting $(La_{1-x},Sr_x)_2CuO_4$ single crystal thin films,Jpn.J.Appl.Phys.,1987,**26**,L524-25 .

70. C.Kittel, Introduction to Solid State Physics,6 th edition,John Wiley & Sons, New York,1988,p.p.178.

71. M.Sera,S.Kondoh,K.Fukuda and M.Sato,Absence of the T-linear term in low temperature specific heat of high-Tc oxide, Bi-Sr-Ca-Cu-O system,Solid State Comm. ,1988,**66**,1101-03;M.Ishikawa, Y.Nakazawa, T.Takabatake, A.Kishi, R. Kato and A.Maesono,Physica C,1989,**153 -155**,1089-91.

72. A.C.Rose-Innes and E.H.Rhoderck, Introduction to Superconductivity, 2 nd. edition, Pergamon Press,Oxford,1978,p.p.128; J.Bardeen, L.N.Cooper and J.R.Schrieffer, Theory of superconductivity, Phys.Rev., 1957, **108** (5), 1175-1204.

73. J.Bardeen,G.Rickayzen and L.Tewordt,Theory of the thermal conductivity of superconductors,Phys.Rev.,1959,**113**,982-994 ; J.E.Smith,D.M. Ginsberg, Thermal conductivity of superconducting tin films in a magnetic field, Phys. Rev.,1968,**167**,345-57 .

74. A.C.Rose-Innes and E.H.Rhoderick,Introduction to Superconductivity, 2 nd. edition,Pergamon Press, Oxford, 1978,p.p.61.

75. K.Kitazawa,T.Atake, M.Sakai, S.Ucida, H.Takagi,K.Kisio,T.Hasegawa, K.Fueki, Y.Saito and S.Tanaka,Specific heat and superconductivity of $(La_{0.925},Sr_{0.075})_2CuO_4$,Jpn.J.Appl.Phys.1987,**26**,L751-53 .

76. Z.G.Khim,S.C.Lee,J.H.Lee,B.J.Suh,Y.W.Park,I.S.Yu and J.C.Park, Superconductivity in single-phase $Y_1Ba_2Cu_3O_{9-x}$ and thermoelectric power measurement, Phys.Rev.,1987,**B36**, 2305-07 .

77. N.Phillips,Low-temperature heat capacities of gallium, cadmium, and copper, Phy.Rev.,1964,**134**(2A), A385-91; R.W.McCallum, D.C.Johnston, C.A.Luengo and M.B.Maple,Superconducting and normal state properties of $Li_{1+x}Ti_{2-x}O_4$ spinel compounds. II. low- temperature heat capacity, J.Low Temp. Phys. 1976,**5**,177-93.

78. J.R.Cooper,B.Alavi,L-W,Zhou,W.P.Beyermann and G.Gruner,Thermoelectric power of some high-Tc oxides, Phys.Rev.,1987, **B35**, 8794-96 .

79. D.R.Tilley and J.T.Tilley, Superfluidity and Superconductivity, John Wiley & Sons, New York,1974, p.p.12 .

80. G.Careri,Order and Disorder in Matter, translated by K.Jarratt,The Benjamin / Cummings Publishing Company,Menlo Park,Califolnia,1984,p.p.61.

81. C.Kittel,Introduction to Solid State Physics,6 th edition,John Wiley & Sons, New York,1988,p.p.127.

82. A.Kapitulnik, M.R.Beasley,C.Castellani and C.DiCastro,Thermodynamic fluctuations in the high-Tc perovskite superconductors, Phys.Rev.,1988,**B37**,537-40 .

83. D.H.Martin,Magnetism in Solids, Iiffe Books,London,1967,p.p.163 .

84. L.N.Mulay and E.A.Boudoaux, Theory and Applications of Molecular Diamagnetism, John Wiley & Sons, New York,1976,p.p.24.

85. A.C.Rose-Innes and E.H.Rhoderick, Introduction to Superconductivity, 2 nd edition,Pergamon Press, Oxford,1978,p.p.65.

86. J.H.Van Vleck, Theory of Electric and Magnetic Susceptibilities, Oxford University, Press, London,1932,p.p.91 .

87. E.Maxwell,Isotope effect in the supercoductivity of mercury, Phy.Rev.,1950, **78**,477;C.A.Reynolds,B.Serin,W.H.Wright and L.B.Nesbitt,Superconductivity of isotopes of mercury, ibid.,1950,**78**, 487; J.W.Garland,Isotope effect in superconductivity,Phy.Rev.Lett. ,1963,**11**,114-19.

88. H.M.Rosenberg,The Solid State,Oxford University Press,Oxford,1988,p.p. 241.

89. E.A.Lynton,Superconductivity, Methuen,London,1969,p.p.93.

90. N.F.Mott.The transition to the metallic state,Phil.Mag.,1961,**6**,287-309; N.F.Mott, Metal-Insulator Transitions,Taylor and Francis, London,1974,p.p.21 .

91. G.M.Harris,Attractive two-body interactions in partially ionized plasmas, Phys. Rev.,1962,**125**,1131-40 .

92. L.H.Thomas, The calculation of atomic fields,Proc.Camb.Phil.Soc.,1927,542-49 .

93. E.Fermi,Eine statistische methode zur bestimmung einiger eigenschaften des atoms und ihre anwendung auf die theorie des periodischen systems der elemente,Z.Phys.,1928 ,**48**,73-79.

94. W.A.Harrison,Electronic Structure and the Properties of Solids,Freeman,San Francisco,1980,p.p.376.

95. H.L.Sriver,Physics of Solids under High Pressure, ed., J.S.Schilling and R.N.Shelton, North-Holland Publishing, Amsterdam,1981,p.p 405.

96. Z.Schlesinger, R.T.Collins, D.L.Kaiser and F.Holtzberg, Superconducting energy gap and normal-state reflectivity of single crystal Y-Ba-Cu-O,Phys. Rev. Lett.,1987,**59**(17)1958-61; X.Wang,T.Nanba,M.Ikezawa,S.Hayashi and H.Komatsu,Optical absorption of $YBa_2Cu_3O_{7-\delta}$ and $ErBa_2Cu_3O_{7-\delta}$ crystals due to interband transition,Jpn.J.Appl.Phys.,1988,**27** (10)L1913-16.

97. C.Kittel,Introduction to Solid State Physics, 6th edition,Jhon Wiley & Sons, New York,1986,p.p.370.

98. C.Kittel,Thermal Physics,Jhon Wiley & Sons,New York,1969,p.p.138.

99. C.Kittel,Introduction to Solid State Physics, 6th edition,Jhon Wiley & Sons, New York,1986,p.p.196.

100. R.W.Guney and E.U.Condon,Quantum mechanics and radioactive disintegration,Phys.Rev.,1929,**33**(2)127-40;B.G.Harvey, Introduction to Nuclear Physics and Chemistry,Prentice-Hall,1969,p.p.194.

101. G.Gamov,Zur quantentheorie des atomkernes,Z.Physik,1928,**51**,204-212.

102. C.Kittel, Introduction to Solid State Physics, 6 th edition,Jhon Wiley & Sons, New York,1986,p. p.234.

103. B.D.Josephson,Possible new effects in superconductive tunneling, Physics Lett.1962,**1**(7)251-53; I.Giaever and K.Megerle, Phys.Rev.,1961,**122**(4) 1101 -11; P.L.Gammel. D.J.Bishop, G.J.Dolan, J.R.Kwo, C.A.Murray, L.F Schnemeyer and J.V.Waszczak,Observation of hexagonally correlated flux quanta in $YBa_2Cu_3O_7$,Phys.Rev.Lett.,1987,**59**(22)2592-95.

104. S.Shapiro,Josephson currents in superconducting tunneling: the effect of microwaves and other observations,Phys.Rev.Lett.,1963,**11**(2),80-82; M.Lee, D.B.Mitzi,A.Kapitulnik and M.R.Beasley, Electron tunneling and the energy gap in $Bi_2Sr_2CaCu_2O_x$,Phys.Rev.,1989, **B39** (1) 801-03 ; G.F.Zharkov, The Josephson tunneling effect in superconductors,Soviet Phys. Uspekhi, 1966, **9**(2) 198-209; C.E.Gough,M.S.Colclough,E.M.Forgan, R.G. Jordan, M.Keene, C.M.Muirhead, A.I.M.Rae,N.Thomas,J.S.Abell and S.Sutton,Flux quantization in a high-Tc superconductor,Nature,1987,**326**,855.

105. M.Imada, On the mechanism of high-Tc superconductivity, J.Jpn. Phys. Soc., 1987,**56**(11)3793-96.

106. F.C.Zhang and T,M,Rice,Effective Hamiltonian for the superconducting Cu oxides,Phy.Rev.,1988,**B**,**37**(7)3759-61.

107. A.C.Rose-Innes and E.H.Rhoderick, Introduction to Superconductivity, 2 nd eddition,Pergamon Press,1978, p.p.153.

108. G.R.Stewart, Heavy-fermion system, Rev.Mod.Phys.,**56**(4)(1984)755-87; M.R. Beasley and T.H.Geballe,Superconducting materials,Physics Today,October, 1964,60-68 .

109. F.P.Bundy and K.J.Dunn,Physics of Solids under Highh Pressure, ed.J.S. Schilling and R.N.Shelton, North-Holland,1981,p.p.40 .

110. A.C.Rose-Innes and E.H.Rhoderick, Introduction to Superconductivity, Pergamon Press, 1978, p.p.126.

111. M.H.Cohen, L.M.Falicov and J.C.Phillips, Superconductive tunneling, Phys. Rev.Lett.,1962,**8**,316-18 .

112. J.A.Pals,On the detectibility of spin-triplet pairing superconductivity with the aid of the Josephson effect,Phys.Lett.,1976,**56A**(5)414-16 ; J.A.Pals,W.von Haeringen and M.H.van Maaren,Josephson effect between superconductors in possible different spin-pairing states, Phys.Rev.,1977,**B15**(5), 2592-99.

113. A.Fujimori, E.Takayama-Muromachi and Y.Uchida,Electronic structure of superconducting Cu oxides, Solid State Commmun.(1987) **63** (9) 857-60; A.Fujimori, E.Takayama-Muromachi, Y.Uchida and B.Okai,Spectroscopic evidence for strongly correlated electronic states in La-Sr-Cu and Y-Ba-Cu oxides,Phys.Rev.1987,**B35**(16)8814-17 .

114. S.Uchida, H.Takagi, H.Ishii, T.Yabe, H.Eisaki,S.Tajima and S.Tanaka, Transport properties of $(La_{1-x},A_x)_2CuO_4$, Jpn.J.Appl.Phys.,1987,**26**(4)L440-42.

115. A.Miller and E.Abrahams,Impurity conduction at low concentrations, Phys. Rev.,1960,**120**(3),745-55 .

116. M.Pollak, Approximations for the ac impurity hopping conduction, Phys. Rev., 1964,**A133**,564-79; M.Pollak,A percolation treatment of dc hopping conduction,J.Non-Crystalline Solids,1972,**11**,1-24 .

117. C.Kittel,Introduction to Solid State Physics, 6 th edition, Jhon Wiley & Sons, New York,1986, p.p.164; S.N.Levine,Quantum Physics of Electronics, Macmillan, New York,1965, p.p.35.

118. C.Kittel,Introduction to Solid State Physics, 6 th edition,Jhon Wiley & Sons, New York,1986, p.p.140, 232.

119. V.L.Ginzburg and L.D.Landau,J.E.T.P,1950,**20**,1064 .

120. A.B.Pippard,The coherence cocept in superconductivity, Physica, 1953, **14**, 765-74 .

121. P.P.Freitas, C.C.Tsuei and T.S.Plaskett, Thermodynamic fluctuations in the superconductor $Y_1Ba_2Cu_3O_{9-\delta}$:Evidence forthree-dimensional superconductivity,Phys.Rev.,1987,**B36**(1)833-39;T.K.Worthington,W.J.Gallagher and T.R. Dinger,Anistropiv nature of high-temperature superconductivity in single-crystal $Y_1Ba_2Cu_3O_{7-x}$, Phys. Rev. Lett., 1987,**59**(10)1160-63 ; T.Enomoto, T.Murakami, M.Suzuki andK.Moriwaki,Jpn.J.Appl.Phys.,1987,**26**(7)L1248-50.

122. A.Goldman,Theories of High Temperature Superconductivity,ed. J.W.Halley, Anderson-Wesley,Redwood City,Calif.,1988,p.p.13;R.J.Cava,B.Batlogg, R.B. Von Dover, D.W.Murply, S.Sunshine, T.Siegrist, J.P.Remeika, E.A.Rietman, S.Zahurak and G.P.Espinosa,Bulk superconductivity at 91 K in single-phase oxygen-deficient perovskite $Ba_2YCu_3O_{9-\delta}$,Phys.Rev.Lett.,1987, **58** (16) 167 - 79.

123. A.Kapitulnik, M.R.Beasley, C.Castellani and C.Di Castro, Thermodynamic fluctuations in the high-Tc perovskite superconductors,Phys. Rev., 1988, **B37**(1)537 -40.

124. D.J.Quinn.III and W.B.Inner.III,Resistance in a superconductor, J.Appl. Phys., 1962,**33**,748-49 .

125. M.B.Maple,Novel type of superconductivity in f-electron systems, Physcs Today, March,72-80 (1986); J.A.Pals,W.van Haeringen and M.H.van Maaren, Josephson effect between superconductors in possibily different spin-pairing states,Phys.Rev.,1977,**B15**(5)2592-99.

126. R.Balian and N.R.Werthamer,Superconductivity with pairs in a relative *p* wave, Phys.Rev.,1963,**131**(4)1553-64 .

127. J.A.Pals,On the detectibility of spin-triplet pairing superconductivity with the aid of the Josephson effect,Phys.Lett.,1976,**56A**(5)414-16 ; J.S.Tsai,Y.Kubo and J.Tabuchi, Phys. Rev. Lett., Josephson effects in the Ba-Y-Cu-O compounds, (1987) **58**(19)1979-81.

128. S.Kita,H.Tanabe,T.Takahashi, M.Tonouchi,Y.Fujiwara and T.Kobayashi, Frequency dependence of ac Josephson effect inpoint-contact (Y,Er)Ba CuO/Nb, J.Jpn. Appl.Phys.,1987,**26**(8)L1353-55.

129. G.Aeppli, A.Goldman, G.Shirane, E.Bucher and M.-Ch.Lux-Steiner, Development of antiferromagnetic correlations in the heavy-fermion system UP_3,Phys.

Rev. Lett.1987, **58**(8) 808-11; D.J.Scalapino,E.Loh,Jr and J.E.Hirsch, *d*-wave pairing near a spin-density-wave instability,Phys.Rev.,1986,**B34**(11)8190-92.

130. J.E.Hirsch,Attractive interaction and pairing in fermion systems with strong on-site repulsion,Phys. Rev. Lett.,1985, **54**(12)1317-20 ; M.T.Beal-Monod, C.Bourbonnais and V.J.Emery,Phys. Rev. **B34**(11) 7716 (1986).

131. C.L.Lin,J.Teter,J.E.Crow,T.Mihalisin,J.Brooks,A.I.Abou-Aly and G.G.Stewart, Observation of magnetic-field-induced superconductivity in a heavy-fermion antiferromagnet:$CePb_3$,Phys.Rev.Lett. (1985)**54** (23)2541-44.

132. A.C.Rose-Innes and E.H.Rhoderick, Introduction to Superconductivity, 2 nd eddition,Pergamon Press,1978,p.p.138; U.Essmann and H.Trauble,The magnetic structure of superconductors,Scientific American,(1971)75-84.

133. A.C.Rose-Innes and E.H.Rhoderick, Introduction to Superconductivity, Pergamon Press, 1978, p.p.137.