

**Zeitschrift:** Helvetica Physica Acta

**Band:** 61 (1988)

**Heft:** 6

**Artikel:** Introduction to the physics of high temperature superconductors

**Autor:** Enz, Charles P.

**DOI:** <https://doi.org/10.5169/seals-115970>

### **Nutzungsbedingungen**

Die ETH-Bibliothek ist die Anbieterin der digitalisierten Zeitschriften. Sie besitzt keine Urheberrechte an den Zeitschriften und ist nicht verantwortlich für deren Inhalte. Die Rechte liegen in der Regel bei den Herausgebern beziehungsweise den externen Rechteinhabern. [Siehe Rechtliche Hinweise.](#)

### **Conditions d'utilisation**

L'ETH Library est le fournisseur des revues numérisées. Elle ne détient aucun droit d'auteur sur les revues et n'est pas responsable de leur contenu. En règle générale, les droits sont détenus par les éditeurs ou les détenteurs de droits externes. [Voir Informations légales.](#)

### **Terms of use**

The ETH Library is the provider of the digitised journals. It does not own any copyrights to the journals and is not responsible for their content. The rights usually lie with the publishers or the external rights holders. [See Legal notice.](#)

**Download PDF:** 17.11.2024

**ETH-Bibliothek Zürich, E-Periodica, <https://www.e-periodica.ch>**

## INTRODUCTION TO THE PHYSICS OF HIGH TEMPERATURE SUPERCONDUCTORS

Charles P. Enz

Département de Physique Théorique, Université de Genève  
1211 Geneva 4, Switzerland

*Dedicated to Professor Georg Busch  
at the occasion of his 80th birthday*

**Abstract.** For the benefit of non-specialist readers the main stations in the history of superconductivity are revisited. Against this background the physical properties believed to be crucial for the new superconductors are then reviewed. In a second step, an analysis of the main theoretical ideas is attempted. This discussion starts with a characterization of the groundstate and continues with an enumeration of the possible excitations. Finally, the proposed pairing and condensation mechanisms are reviewed. No attempt of completeness is made, neither with regard to the experimental results nor to the theoretical models. The aim is to get a glimpse at the physics behind the enormous flow of information in this new field of research.

### 1 - The early history of superconductivity

In 1908 Kamerlingh Onnes had succeeded to liquefy helium at a temperature of 4.2 degrees Kelvin (K), that is at  $-268.9C$ . Three years later he discovered that at this temperature mercury completely lost its electrical resistance as shown in Fig.1<sup>1</sup>. In the course of the years many other metals were discovered to be superconductors, they are listed in Fig.2<sup>2</sup>.

It turned out, however, that zero resistance is not a sufficient condition for superconductivity. In 1933 Meissner and Ochsenfeld discovered that a magnetic field  $H$  is expelled from a metal when it is in the superconducting state, i.e. when its temperature  $T$  is below the critical temperature  $T_c$ , provided that  $H$  is also smaller than a critical field  $H_c$ . The two situations of expulsion are shown in Fig.3<sup>1</sup>.

The explanation of this "Meissner effect" is that an external magnetic field  $H < H_c$  induces a surface current distribution  $j$  perpendicular to the field.  $j$ , in turn produces a field that exactly compensates  $H$ , leading to a perfect diamagnetism,  $\chi = -(4\pi)^{-1}$ . The existence of a critical field  $H_c$  is then understood as due to a critical value of the surface current density, above which superconductivity breaks down.

While further phenomenological understanding progressed steadily<sup>1</sup>, the breakthrough in the microscopic theory came only in 1957 with the famous work of Bardeen,

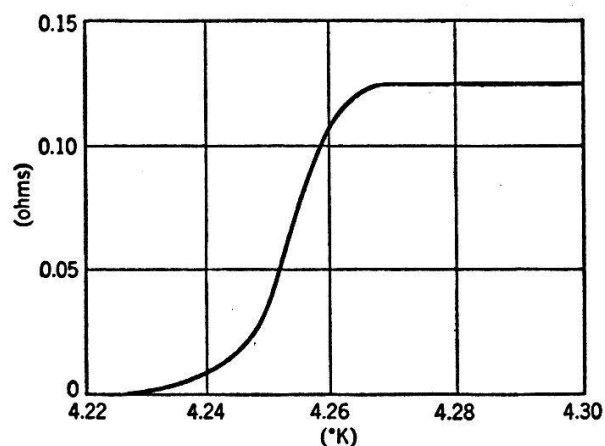


Fig.1: Electrical resistance versus absolute temperature for mercury.

H																			He
Li	Be											B	C	N	O	F	Ne		
Na	Mg											Al	Si	P	S	Cl	Ar		
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr		
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe		
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn		
Fr	Ra																		

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
Ac	Th	Pa	U	Np	Pu								

<b>Al</b>	Superconducting	<b>B</b>	Nonmetallic elements
<b>Si</b>	Superconducting under high pressure or in thin films	<b>F</b>	Elements with magnetic order
<b>Li</b>	Metallic but not yet found to be superconducting		

Fig.2: Periodic table of elements and low-temperature properties.

Cooper and Schrieffer (BCS)<sup>3</sup>. The idea of BCS theory is that electrons form pairs with zero momentum (and also zero angular momentum), and these "Cooper pairs" condense at

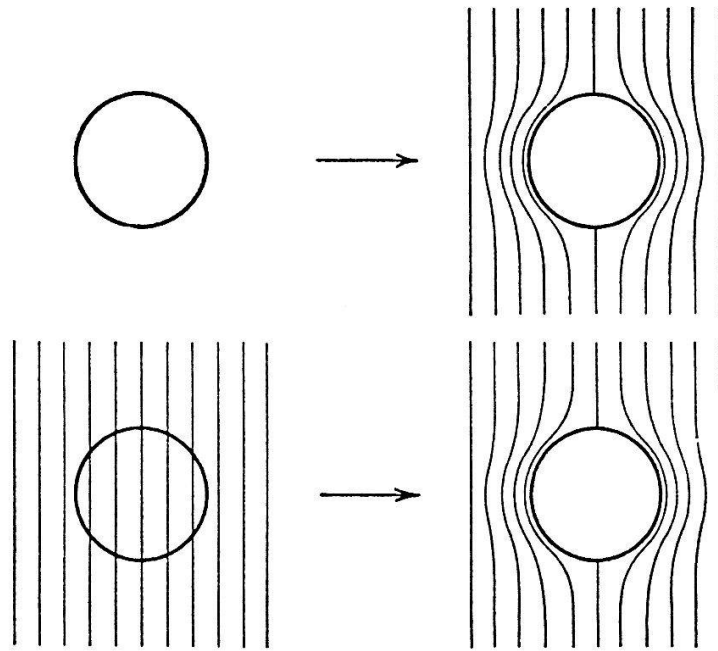


Fig.3: Field expulsion from a superconductor. Above:  $T < T_c, H = 0 \rightarrow H_c > H > 0$ . Below:  $H_c > H > 0, T > T_c \rightarrow T < T_c$ .

$T_c$  into the superconducting state. This condensation of Cooper pairs is analogous to the Bose-Einstein condensation of "bosons" (see below), e.g. helium atoms<sup>1</sup>. The difference, however is that in BCS theory condensation occurs simultaneously with pairing.

Pairing requires an attractive force between the electrons which in BCS theory is mediated by the interaction of the electrons with the vibrations of the crystal lattice, the phonons<sup>2</sup>. The resulting effective electron-electron interaction  $V$  determines the critical temperature according to the equation<sup>3</sup>

$$T_c = 1.14\omega e^{-1/N(0)V}. \quad (1)$$

Here  $\omega$  is a limiting phonon frequency (Debye frequency) and  $N(0)$  the density of states at zero energy, counted from the filling level (Fermi energy) of the electrons.  $T_c$  and  $\omega$  are measured in energy units.

Since phonon frequencies vary with the ionic mass  $M$  as  $M^{-1/2}$ , Eq.(1) gives the same  $M$ -dependence for  $T_c$ . As noted by BCS, this explains the isotope effect which had been discovered 7 years earlier<sup>4</sup>. It was soon realized, however, that the  $M$ -dependence of  $T_c$  is considerably more complicated because not only  $\omega$  in Eq.(1) but also  $V$  depend on the ionic mass. This latter dependence essentially comes from the Coulomb repulsion which was not mentioned above while the part of  $V$  mediated by the phonons is practically independent of  $M$ .

Pair breaking requires an energy  $2\Delta$  where  $\Delta(T)$  is the "order parameter" which depends on the temperature, and  $\Delta_0 = \Delta(0)$  is the gap in the excitation spectrum. BCS

theory gives the following relations for  $\Delta(T)$  near  $T_c$  and at  $T = 0$ :

$$\Delta(T) = 3.06T_c(1 - T/T_c)^{1/2}, \Delta_0 = 1.76T_c. \quad (2)$$

The entire curve  $\Delta(T)$  is represented in Fig.4 <sup>3</sup>.

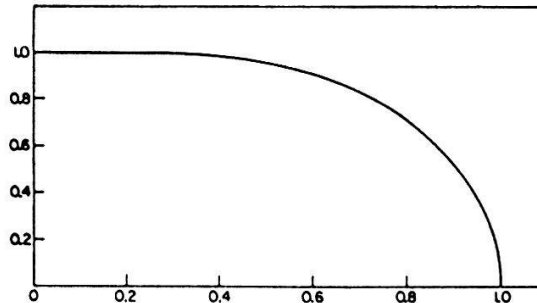


Fig.4:  $\Delta(T)/\Delta_0$  versus  $T/T_c$ .

## 2 - The search for new superconductors

The obvious interest of superconductivity, namely to allow electrical currents without loss, as well as the intrinsic interest led to a competitive search for materials with ever higher  $T_c$ 's and/or higher  $H_c$ 's. After the elements shown in Fig.2, many alloys were tested, among which NbTi became of particular importance for cryogenic applications. But besides alloys, interest turned to compounds with precise stoichiometry, first binaries then ternaries and quaternaries.

The most important binary superconductors were the so-called A15 compounds discovered in 1954, namely  $V_3Si$  with a  $T_c$  of 17K and  $Nb_3Sn$  which has  $T_c = 18K$  <sup>5</sup>. Apart from the mentioned alloy NbTi,  $Nb_3Sn$  has been the main material from which wires were produced.  $Nb_3Ge$  which had the highest  $T_c$  of 23.2K until the recent discovery of the "high- $T_c$  superconductors" (see below), had proven too difficult to be produced on an industrial scale.

Two classes of ternary compounds were subsequently found to contain some interesting superconductors among their members, first the "Chevrel phases" called after the French discoverer of this class. The first superconductors in this class were discovered by Matthias in 1972 <sup>6</sup>, namely  $M_xMo_6S_8$  with  $M = Cu, Ag, Zn, Sn, Pb$ . While the  $T_c$ 's are all lower than 15K, some of the Chevrel superconductors such as  $PbMo_6S_8$  have the highest  $H_c$ 's, as is seen in Fig.5 <sup>7</sup> which reviews the materials discussed so far.

The second class of ternaries are the "heavy-fermion compounds", so called because they have a linear electronic specific heat at low temperatures <sup>2</sup>

$$c_v = \gamma T \quad (3)$$

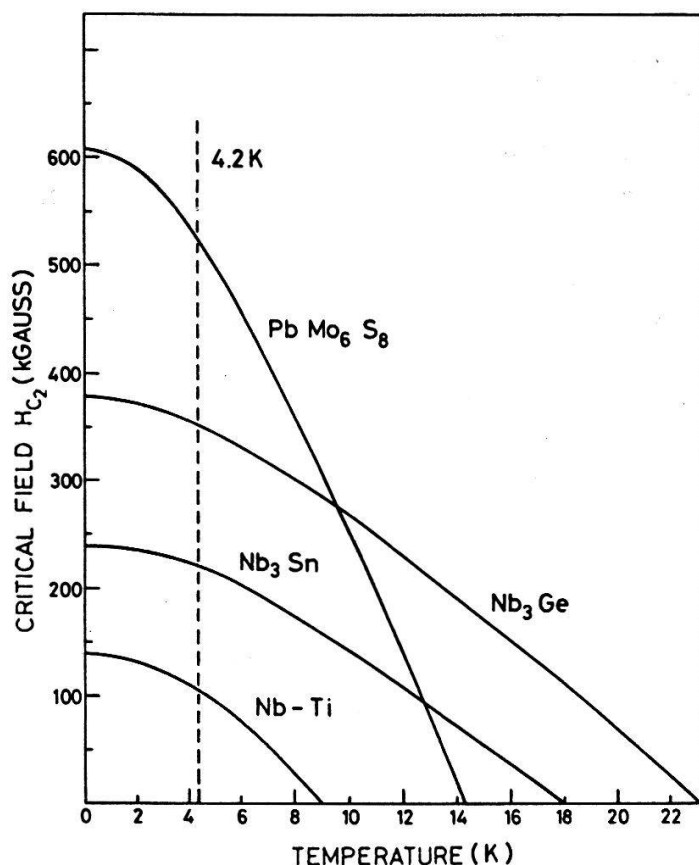


Fig.5: Upper critical field  $H_{c2}$  versus  $T$  for the most interesting "old" superconductors.

with a  $\gamma$ -value 100 to 1000 times larger than for other metals, indicating an anomalously large effective mass of the conduction electrons. The first superconducting heavy fermion compound  $CeCu_2Si_2$  was discovered by Steglich in 1979<sup>8</sup>. However, it has a  $T_c$  of only about 0.5K.

A quite different type of superconductor was discovered in 1980, namely an organic compound of quasi-linear structure with the abbreviated name of  $(TMTSF)_2PF_6$ <sup>9</sup>. Although this substance became superconducting only under high pressure, some 12kbar, and with a  $T_c$  of about 1K, this discovery showed for the first time that superconductivity is not restricted to ordinary metals. This is all the more important in view of the "high- $T_c$  superconductors" discovered since and also because many other quasi-linear organic substances have been found since to be superconducting at atmospheric pressure. The latest discovery in this class was announced at the Interlaken Conference on high- $T_c$  superconductivity (March, 1988) by a Japanese group who found a  $T_c$  of 10K, which is an increase of a factor 10!

The suggestion that organic molecules could be superconducting, however, is much older. Indeed, in 1964 Little<sup>10</sup> discussed a model molecule consisting of a spine to which many side chains are attached. Based on BCS theory he concluded that such a

system had a phonon spectrum allowing  $T_c$ 's much higher than room temperature! Unfortunately, his work did not obtain the attention it is retrospectively thought to have deserved.

During three decades the barrier of  $T_c \sim 23K$  had not been broken, in spite of considerable efforts worldwide. This barrier thus became psychological, and various theoretical attempts were made to make plausible that there was an intrinsic limit<sup>11</sup>. It therefore came as a shock when in 1986 J. G. Bednorz and K. A. Müller from the IBM Zurich laboratory announced the discovery of a  $Ba - La - Cu - O$  compound with a  $T_c$  of some  $30K$ <sup>12</sup>, still close enough to the barrier to be credible! The next decisive step came less than a year later when the group of C. W. Chu from the University of Houston (Texas) and of M. K. Wu from the University of Alabama discovered the  $Y - Ba - Cu - O$  compound with  $T_c \sim 93K$ <sup>13</sup>. This meant superconductivity above the boiling point of nitrogen ( $-195.8C$ ) which now could be substituted for the expensive helium as a coolant.

### 3 - The new "high-temperature" superconductors

The new materials discovered by Bednorz and Müller<sup>12</sup> and by Chu and his group<sup>13</sup> are quaternaries whose crystal structure is built up from unit cells which are elongated along the c-axis and have an essentially quadratic base in the  $a - b$  plane. The first class consists of the lanthanum compounds  $La_{2-x}M_xCuO_4$  with variable impurity content  $x \leq 0.15$  and  $M = Ba, Sr$  while the second is the so-called "1-2-3 compound"  $YBa_2Cu_3O_{6+x}$  with variable oxygen content  $x \leq 1$ . Oxygen loss is also observed in the lanthanum compound. Therefore, both materials have to be handled in a controlled atmosphere which, obviously, causes problems in technical applications.

Among the four atomic species of these compounds it is the copper-oxygen subsystem which in both materials is responsible for the interesting physics: Each  $Cu$  is the centre of an octahedron of  $O$ 's which is elongated in the c-direction. In the 1-2-3 compound there are additional copper and oxygen atoms which alternate in chains along the b-axis whose role is still not elucidated. In both materials there is a structural phase transition at a temperature far above  $T_c$  and which has no obvious connection with superconductivity. In the lanthanum compounds the transition, with decreasing temperature, is from tetragonal to orthorhombic, as shown in Fig.6<sup>14</sup>, in the 1-2-3 compound it is the inverse, as seen in Fig.7<sup>15</sup>.

More importantly, the  $x = 0$  version is insulating and antiferromagnetic (AF) both, in the pure lanthanum compound  $La_2CuO_4$ <sup>16</sup> and in  $YBa_2Cu_3O_6$ <sup>17</sup>. It is only with increasing  $x$  that the metallic state and superconductivity set in, as seen in the phase diagram of Fig.8<sup>18</sup>, valid for the lanthanum compounds. In the AF state the specific heat does not show the linear term of Eq.(3) which is typical of metallic behaviour. But a finite  $\gamma$ -term is present in the superconducting state, as is seen in Fig.9<sup>18</sup>. This is surprising since, because of the gap of Eq.(2), a superconductor behaves thermally like an insulator at low temperatures.

Another surprising feature is found in the temperature dependence of the electrical resistivity  $\rho$  in the normal (non-superconducting) state at low temperatures<sup>2</sup>. Note



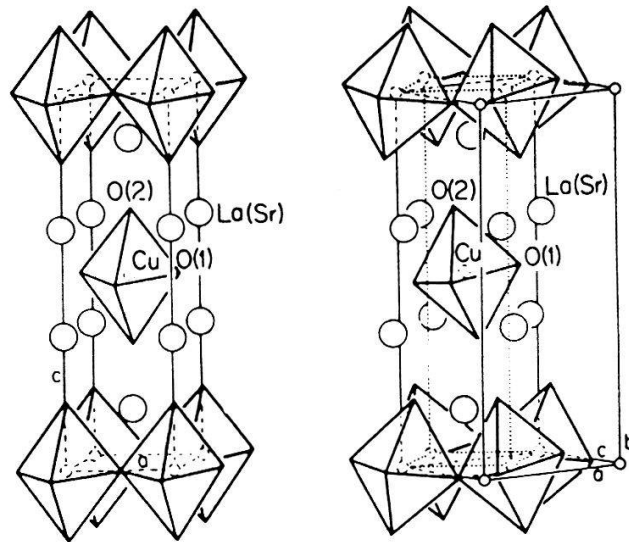


Fig.6: Unit cells of tetragonal (left) and orthorhombic (right)  $La_{1.85}Sr_{0.15}CuO_4$ .

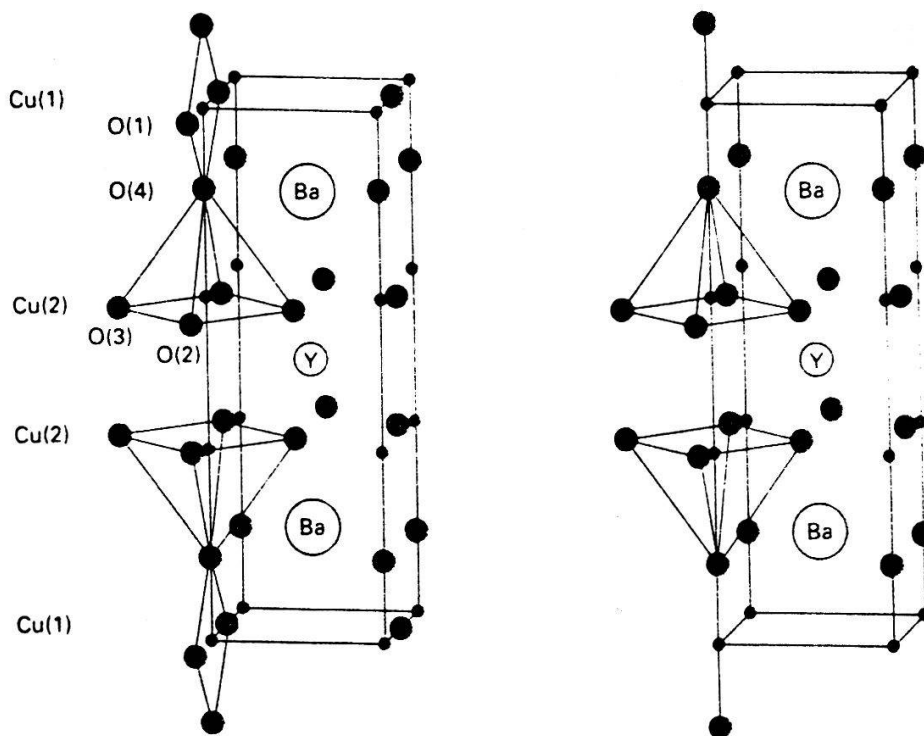


Fig.7: Unit cells of orthorhombic (left)  $YBa_2Cu_3O_7$  and tetragonal (right)  $YBa_2Cu_3O_6$ .

that normal metallic behaviour below  $T_c$  may be achieved by applying a magnetic field  $H > H_c$ . One finds that in the  $c$ -direction the material is semiconducting,  $\rho \propto 1/T$ , while



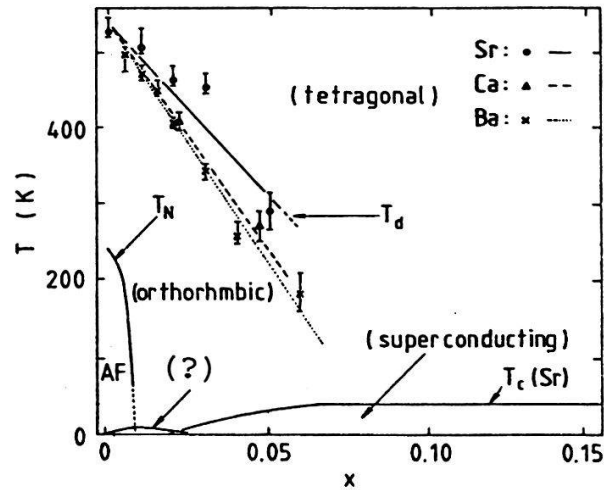


Fig.8: Phase diagram of  $La_{2-x}M_xCuO_4$ ,  $M = Sr, Ca, Ba$ .

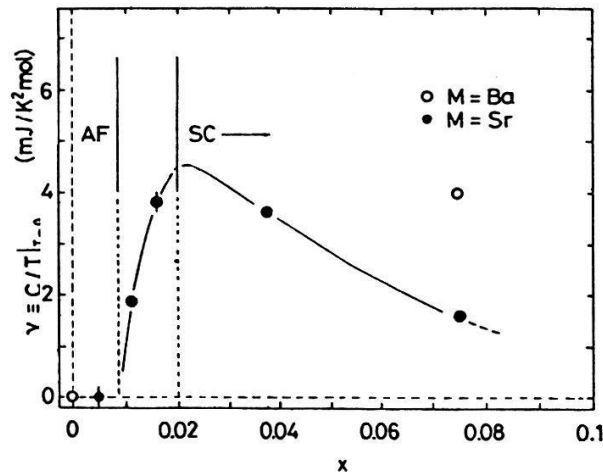


Fig.9: Linear specific heat coefficient  $\gamma$  versus  $x$  of  $La_{2-x}M_xCuO_4$ ,  $M = Ba, Sr$ .

in the  $a - b$  plane  $\rho \propto T$ . The latter  $T$ -dependence is different from the usual law  $\rho \propto T^2$  found for metals at low temperatures. Plotting the two empirical findings as  $T\rho$  versus  $T^2$  they are both represented by straight lines, as shown in Fig.10<sup>19</sup>.

At the Interlaken conference, two new classes of superconductors with still higher  $T_c$ 's were announced, both being quinary compounds. The first is a  $Bi - Sr - Ca - Cu - O$  system with  $T_c \sim 110K$ , the second consists of  $Tl - Ca - Ba - Cu - O$  and has  $T_c \sim 125K$ . Again there is a copper-oxygen subsystem arranged in square lattices perpendicular to the  $c$ -axis and which seems to be responsible for superconductivity. But the unit cell of these quinarys is larger and contains more atoms than in the quaternaries.

Apart from their high  $T_c$ -values these new compounds are of great interest because of their stability against loss of oxygen. Nevertheless, we will not discuss them

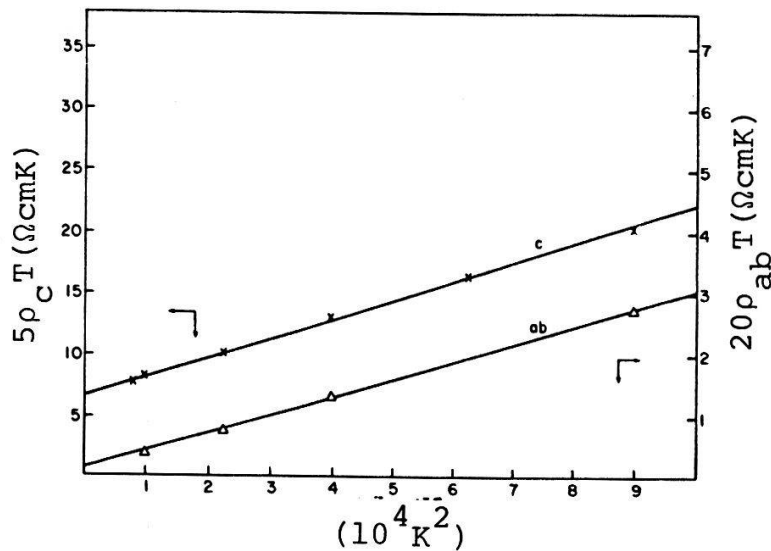


Fig.10: Resistivity data for  $YBa_2Cu_3O_{7-y}$  plotted as  $\rho T$  versus  $T^2$ .

further. Suffices it to observe that, compared to the "old" binary superconductors the gain in  $T_c$  today is a factor of 5 which, however, is still short of the factor of 10 achieved in the quasi-linear organic compounds mentioned earlier.

The standard preparatory procedures produce these new substances in a ceramic form consisting of superconducting grains separated by insulating boundaries and with a strong tendency to form twins. In addition, there are the imperfections and/or impurities characterized by the stoichiometric variable  $x$  introduced earlier which create disorder in the crystal lattice. As a result, the Meissner effect is in general not complete, meaning that there is partial and often not reversible penetration of the magnetic field.

Superconductivity in these ceramics is thought to come about by tunneling of the electric current across the barriers separating the grains as in a Josephson junction<sup>2</sup>. The physics may then be described in terms of a phase angle  $\phi_i$  for each grain  $i$  and of a Hamiltonian<sup>20</sup>

$$H = - \sum_{\langle i,j \rangle} J_{ij} \cos(\phi_i - \phi_j - A_{ij}). \quad (4)$$

Here  $A_{ij} = (2\pi/\Phi_0) \int_i^j \vec{A} \cdot d\vec{l}$ ,  $\vec{A}$  being the vector potential describing an external magnetic field and  $\Phi_0$  the flux quantum.

This granular structure and hence also the physics described by Eq.(4) are, however, not intrinsic properties. Indeed, it has been possible to produce single crystals of these materials. Elimination of twinning turns out to be more difficult and is therefore considered by some researchers as intrinsic in the sense that they think twin boundaries to be essential for superconductivity. Here we will not pursue this point of view further, however, but turn to the theoretical attempts to explain the intrinsic properties.

#### 4 - Theoretical description of the groundstate

Although old arguments against an electron-phonon mechanism to explain the high  $T_c$ 's of the new superconductors have been mentioned<sup>11</sup>, it cannot be excluded that at least some specific phonon modes may play a role. As was discussed earlier, the existence of an isotope effect would be a clear indication of this. Such experiments have been performed, both with the lanthanum and with the yttrium compounds by replacing the natural isotope  $^{16}\text{O}$  by  $^{18}\text{O}$ . In both cases the shift of  $T_c$  was non-zero but less than  $1\text{K}$ <sup>21</sup>. This leaves the question rather undecided.

As already mentioned, the essential physics happens in the copper-oxygen subsystem. Therefore, the valencies which these atoms assume in the crystal are of primary importance. The electronic configurations of the neutral atoms are

$$\text{Cu}^0 = (\text{Ar})3d^{10}4s^1, \text{O}^0 = (\text{Be})2p^4 \quad (5)$$

where  $(\text{Ar})$  and  $(\text{Be})$  are, respectively, the configurations of argon and beryllium. It is thus seen that  $\text{Cu}^+ = (\text{Ar})3d^{10}$  and  $\text{O}^{2-} = (\text{Be})2p^6$  are closed-shell configurations, the latter being particularly stable because it corresponds to neon. Oxygen therefore favours the valency 2-.

In the pure ( $x = 0$ ) lanthanum compound  $\text{La}_2\text{CuO}_4$ ,  $\text{La}$  acts as a donor of one electron. And since the configuration in the  $a - b$  planes is  $\text{CuO}_2$ , copper enters with the valency 2+. In this count the oxygens  $\text{O}(2)$  in Fig.6, situated above and below  $\text{Cu}$ , then have valency zero which explains the instability against loss of oxygen mentioned earlier. In the  $\text{Y} - \text{Ba} - \text{Cu} - \text{O}$  compound the situation is somewhat more complicated<sup>22</sup>.

Of course, the above argument is too naive since it does not take into account possible covalent contributions to the binding. In other words, it treats the electrons as point charges and does not make use of the finite extension of their wave function. The main result of the above reasoning, however remains valid, namely that in the "pure" ( $x = 0$ ) state copper enters with valency 2+. But according to Eq.(5),  $\text{Cu}^{2+}$  contains one hole (missing electron) and hence has a spin of  $1/2$ . The observed AF state mentioned earlier then means that the spins of the copper atoms in the square lattice of the  $a - b$  planes alternate, as shown in Fig.11, and there is also an alternation in the consecutive  $a - b$  planes<sup>16,17</sup>.

From the theoretical point of view, this AF spin arrangement of the "pure" compounds has to be considered as the "groundstate" of the electronic system. The  $M$ -impurities in  $\text{La}_{2-x}\text{M}_x\text{CuO}_4$  and the surplus- $\text{O}$  in  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  measured by  $x$  then create excitations in the form of excess holes which for small  $x$  must be localized since, according to the phase diagram (Fig.8 in the lanthanum case) the systems are still insulating.

The first energy band calculations for the new superconductors, on the other hand, showed metallic behaviour even for  $x = 0$ . This is seen in the density of states shown in Fig.12<sup>23</sup> which is non-zero at the Fermi energy  $E_F$  and therefore represents a metal<sup>2</sup>. This shows that band structure calculations, which involve a one-electron approximation, do not properly take into account the strong correlations between electrons due to the localization of the holes.

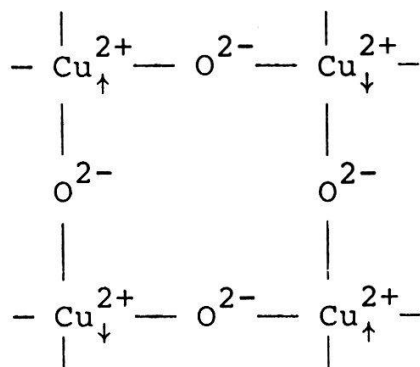


Fig.11: Antiferromagnetic spin arrangement of  $Cu - O$  lattice in the  $a - b$  planes.

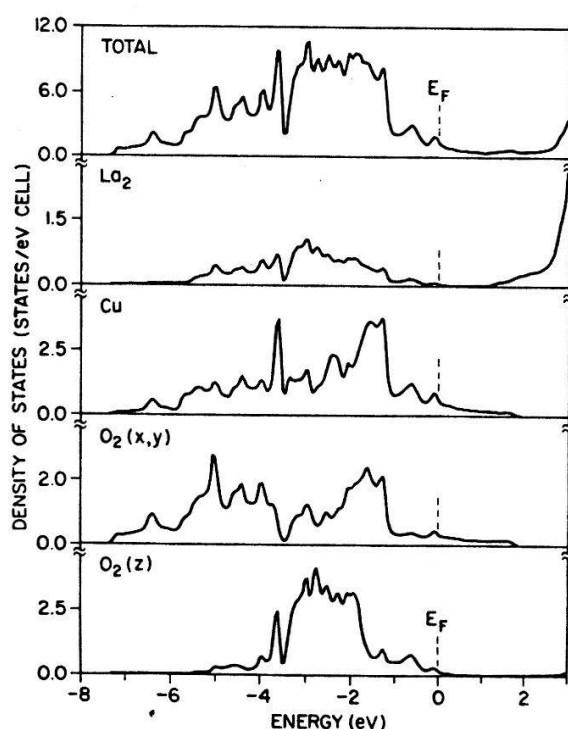


Fig.12: Calculated total and projected densities of states for  $La_2CuO_4$ .

However, these calculations are better than it may appear from the above remarks. Indeed, the almost quadratic form of the Fermi surface shown in Fig.13<sup>23</sup> implies a "nesting" behaviour of the electron pair states leading to an instability against formation of a spin density wave (SDW)<sup>2</sup>. This SDW is commensurate with the crystal lattice. Indeed, its wavelength is twice the  $Cu - Cu$ -distance in the  $a - b$  planes and describes the AF spin arrangement of Fig.11. The important fact, however, is that this instability opens an energy gap at  $E_F$  which transforms the system from metallic to insulating<sup>24</sup>.

A similar situation is observed in the yttrium compound. Indeed, if the band calculations are done for the two spin directions separately, the result for an AF arrangement correctly yields insulating behaviour<sup>25</sup>.

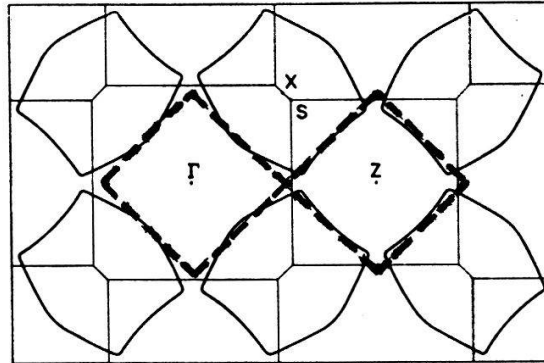


Fig.13: Calculated Fermi surface for  $La_2CuO_4$ . Dashed lines: Perfect nesting obtained in tight-binding approximation.

The spin configuration shown in Fig.11 may be described by a 2-dimensional Heisenberg model defined by the Hamiltonian<sup>2</sup>

$$H_{spin} = J \sum_{\langle i,j \rangle} \vec{S}_i \cdot \vec{S}_j, J > 0 \quad (6)$$

where  $\vec{S}$  is the vector operator for spin 1/2 and the sum runs over nearest-neighbour sites  $i, j$  of the  $Cu$ -lattice. The determination of the ground state of the model described by Eq.(6) is an old problem going back to the thirties. Indeed, the AF arrangement which has long-range order, is very close in energy to a spin configuration without long-range order in which neighbouring spins  $i, j$  are paired off into a singlet state. The latter is obtained by operating on the vacuum state with

$$b_{i,j}^+ = 2^{-1/2}(c_{i\uparrow}^+ c_{j\downarrow}^+ - c_{i\downarrow}^+ c_{j\uparrow}^+) \quad (7)$$

where  $c_{i\sigma}^+$  is the creation operator for a hole with spin  $\sigma$  (up or down) on the copper site  $i$ .

These singlet "dimers" (two-component objects) created by the operator of Eq.(7) are called "valence bonds" by Anderson<sup>26</sup>. In 2 dimensions such a non-ordered spin configuration has to be expected on a triangular lattice because an alternating spin configuration is not possible on a triangle: Two neighbouring spins must be parallel which, according to Eq.(6) requires a positive amount of energy and therefore is unfavourable. This situation is called "frustration".

In the real lanthanum or yttrium systems the above idealized situation is of course modified in many ways. First, the  $Cu$ -lattice is square, not triangular so that

frustration is not a necessity. But, second, the Heisenberg model (6) is not an accurate description of the localized charges on the *Cu*-sites. The last-mentioned feature is better described by the planar Hubbard model <sup>27</sup>

$$H_{charge} = -t \sum_{\langle i,j \rangle \sigma} c_{i\sigma}^{\dagger} c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow}. \quad (8)$$

In this formula the first term describes hopping of the holes between neighbouring sites *i, j* while the second term is a simplified form of the Coulomb repulsion between a spin-up and a spin-down hole on the same site *i*,  $n_{i\sigma}$  being the number operator of a hole at *i* with spin  $\sigma$ . Note that holes with parallel spins cannot occupy the same site because of the Pauli principle.

The physics described by the two models (6) and (8) is very similar, at least for  $|t| \ll U$  and near half-filling (Fig.14). Indeed, a canonical transformation of the form  $\exp(S)H_{charge}\exp(-S)$  produces, among many other terms,  $H_{spin}$  with  $J = 4t^2/U$ . Among these other terms there are also next nearest neighbour frustration terms which destroy a possible AF long-range order, but an alternative mechanism having the same effect are lattice distortions <sup>26</sup>, produced, e.g. by metal impurities or surplus oxygen,  $x > 0$ . In addition, there must be some coupling between adjacent *Cu - O* layers.

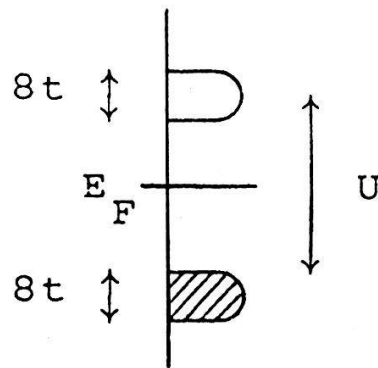


Fig.14: Energy bands of Hubbard model for strong repulsion and half filling.

The above arguments make a valence-bond groundstate quite plausible, at least for  $x > 0$ . Since an AF square lattice may be divided into two sublattices with up and down spins only, there is an enormous number of configurations in which all up and down spins (not only neighbours) are paired into singlets. For the groundstate, linear combinations of all these configurations may then be considered. This leads to Anderson's notion of "resonating valence bond" (RVB) <sup>26</sup> which expresses the fact that a valence bond cycle in one configuration may switch, leading to another configuration and back again, see Fig.15.

Based on arguments in favour of a given groundstate - RVB or AF or metallic - any theoretical model must then introduce the appropriate excitations leading to conduction, as well as a mechanism of condensation describing superconductivity. The challenge



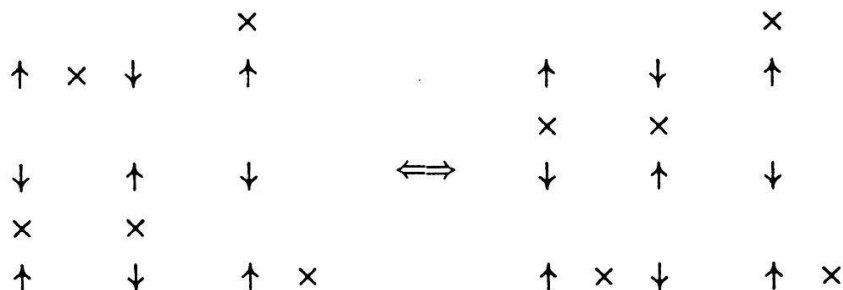


Fig.15: Nearest-neighbour valence bonds, marked by crosses. The left and right configurations differ in a 3-bond cycle.

of course lies in the problem of explaining the unusually high values of  $T_c$ . Here the results are still vague.

### 5 - Theoretical models for the excitations

According to Anderson<sup>26</sup>, two types of excitations may be generated on top of the RVB groundstate. The simplest one which does not require the introduction of additional charges (holes), is just an isolated unpaired spin  $\sigma$  (up or down), as shown in Fig.16a. By definition, this excitation called "spinon" does not carry a charge. It is essentially, i.e. in a purely ionic approximation, just a  $Cu_{\sigma}^{2+}$ . Since this single spin may brake up a neighbouring valence bond and pair with one of the former partners, it is obvious that a spinon can move through the  $Cu$  lattice very freely. Having spin 1/2, a spinon is a fermion, that is it obeys the Pauli exclusion principle and hence fills up the lowest energy states defining a pseudo-Fermi energy<sup>26</sup>.

The second type of excitation of the RVB model is a single charge on a  $Cu$ -site, called "holon". Excess charges are introduced into the lattice by doping (in the lanthanum case) or by excess oxygen (in the yttrium case), that is by having  $x > 0$ . In an ionic approximation, a holon is obtained by the reaction



see Fig.16b. Here the paired up and down spins on the  $Cu^{3+}$  requires some comment. Indeed, in the free atom such a configuration is excluded by Hund's rule which energetically favours electrons with parallel spins in different orbitals. In the ionic crystalline environment of the systems in question, however, the crystal field energy compensates the Hund's rule energy, both being of the order of  $0.5eV$ <sup>28</sup>. More seriously, the existence of  $Cu^{3+}$  in these materials is not generally accepted. Experimentally, it is indeed rather difficult to determine the  $Cu$ -valence<sup>22</sup>. The last mentioned reference, however, contains convincing data supporting the presence of  $Cu^{3+}$ , see also Ref.15.



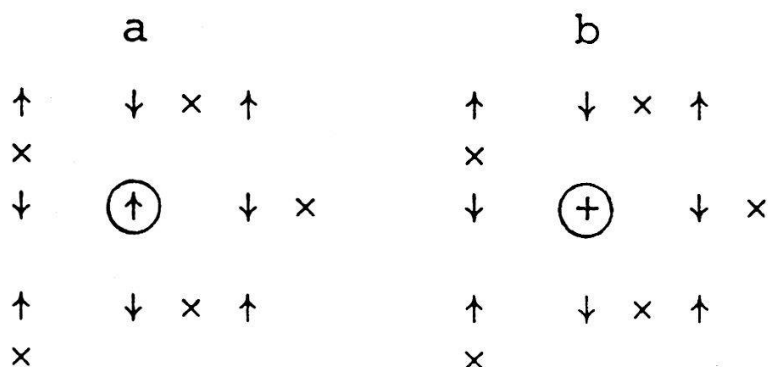


Fig.16: Unpaired spin or "spinon"  $Cu_{\uparrow}^{2+}$  (a) and excess hole or "holon"  $Cu_{\uparrow\downarrow}^{3+}$  (b) in a valence-bond configuration.

The key property following from Eq.(9) is that a holon has spin zero and hence is a boson. In contradistinction to fermions, bosons may pile up in a given state. In particular, at  $T = 0$  they may all condense into the zero-momentum state which is the Bose-Einstein condensation mentioned earlier. According to some authors<sup>29,30</sup> the holons come in two versions, "up" and "down", resulting in two condensates. This is because the AF square lattice consists of two sublattices, an "up" and a "down" one, as mentioned before.

As Eq.(9) shows, a spinon and a holon interact by the exchange of a hole. This relation may be viewed as "supersymmetry", grouping spinon and holon into "superpartners"<sup>31</sup>. More importantly, it is this interaction which according to Anderson is responsible for the linear temperature dependence of resistivity,  $\rho \propto T$ , mentioned earlier. The argument goes as follows<sup>19</sup>: Scattering among fermions leads to a  $T^2$ -law at low temperatures; but in fermion-boson scattering the Pauli principle is inoperative which lowers the power of  $T$  by one. It should be noted, however, that this linear law may also be explained without invoking RVB theory<sup>32</sup>.

The main weakness of RVB theory is that it does not explicitly introduce the oxygen ions (see Fig.11). As a consequence, it is unable to account for hole hopping between  $Cu$  and  $O$  sites which is essential, among other things, for the oxygen loss mechanism mentioned earlier. The same criticism applies to theories based on the simple, i.e. non-extended, Hubbard model<sup>33-36</sup>.

Alternative theoretical models either assume mobile  $Cu$ -holes in an AF background hopping via the  $O$ -neighbours<sup>37-40</sup> or mobile  $O$ -holes hopping via neighbouring  $Cu$ -sites<sup>41-43</sup> or band holes interacting with the commensurate SDW mentioned earlier<sup>44</sup>. In all these models superconductivity requires a pairing mechanism in order to obtain boson-like objects from the holes which are fermions. This problem will be addressed in the last section.

## 6 - Pairing and condensation mechanisms

In RVB theory two different condensation mechanisms have been proposed. The first is the holon condensation<sup>29,30,45</sup> already mentioned. There is, however, a difference not mentioned above between this process and Bose-Einstein condensation of a gas of free bosons in 3 dimensions. Indeed, the holons are localized on the *Cu*-ions and, in addition, are restricted to 2 dimensions. For both these reasons holon condensation requires some kind of attractive interaction which may be mediated either by spinon exchange or by interlayer coupling<sup>29</sup>.

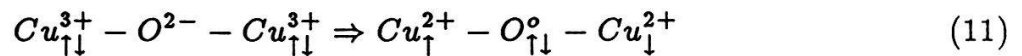
The second mechanism discussed in the framework of RVB theory is condensation of the valence bonds of Eq.(7), meaning that the order parameter of Eq.(2) is now defined as<sup>33,30</sup>

$$\Delta = 2^{1/2} \langle b_{i,j} \rangle . \quad (10)$$

This  $\Delta$  is degenerate with respect to the "up" and "down" sublattices, as well as to the a- and b-directions<sup>30</sup>. Since there are also "up" and "down" holon condensates the question may be asked whether the two condensation mechanisms discussed here are equivalent in a supersymmetric sense.

In the models based on the assumption of hopping *Cu*-holes, two different pairing mechanisms have been proposed. In the first, the AF background acts like a "spin bag" which preferentially attracts two holes with opposite spin on nearest-neighbour sites and thus leads to pairing<sup>28,37,38</sup>. Superconductivity then is obtained by a conventional BCS formalism<sup>37,38</sup>.

The second type of model makes use of the fluctuating valence reaction<sup>15,39,40</sup>

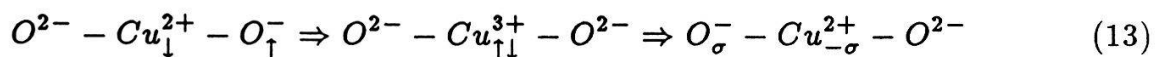


which also explains the oxygen loss mechanism because of the neutral oxygen. This reaction leads to a coupling between the two holes on the  $Cu^{3+}$  and the two holes on  $O^{\circ}$ . Approximating the latter by a doubly charged spin-zero boson, the zero-momentum projection of this interaction has the form<sup>40</sup>

$$H_{int} = W \sum_k a_{k\uparrow}^+ a_{-k\downarrow}^+ b + herm.conj. \quad (12)$$

Here  $a_{k\sigma}^+$  is the creation operator for a hole of momentum  $k$  and  $b$  the annihilation operator for the doubly charged boson on the  $O$ -site. The coupling constant  $W$  may be expressed in terms of an extended Hubbard model in which the  $O$ -ions are explicitly taken into account<sup>46</sup>. Treated in strong coupling approximation this model yields a  $T_c$  which, in contradistinction to most of the other proposals, does not have the exponential upper bound inherent in all the expressions of the type of Eq.(1).

In Emery's model<sup>41-43</sup>, pairing of the hopping  $O$ -holes is obtained from the attraction resulting from the exchange of a hole between two neighbouring  $O$ -ions via the intermediate  $Cu$  site which here is assumed to be delocalized<sup>41</sup>. This process is in a certain sense the inverse of the fluctuating valence reaction (11). It may indeed be written as the 2-step process



where, however,  $Cu^{3+}$  is supposed to be delocalized. Again the coupling constant for this reaction follows from an extended Hubbard model<sup>41</sup>. But superconductivity is derived in the framework of conventional BCS theory.

Pairing of the band-holes in Schrieffer's model is again based on a mechanism of spin-bag attraction<sup>44</sup>: Nesting results in a commensurate SDW and in localization, as discussed earlier. An added hole interacts with the SDW by creating its own spin bag which then attracts a second hole. Again superconductivity is derived along the lines of BCS.

Pairing in the 2-dimensional nearly half-filled Hubbard model with strong on-site repulsion also deserves some comments. While the valence-bond pairing of Eq.(10) is obtained in a mean-field approximation<sup>33,30</sup>, more sophisticated treatments lead to d-state pairing<sup>34,35</sup>. However, a direct computer solution for relatively small numbers of sites does not lead to any pairing at all<sup>36</sup>. This result is intuitively satisfying since, naively, it is hard to see how pairing should come about with only repulsive interactions. But, of course, very strong repulsion combined with the Pauli principle may well force the holes to live in pairs!

Finally, it should be remembered that high- $T_c$  superconductivity depends crucially on doping,  $x > 0$ , either with metal impurities or with excess oxygen, and that therefore disorder is an intrinsic property. Theory, of course, should account for this fact which leads to the notion of a "superconducting glass"<sup>47</sup> and may even be the key to high  $T_c$ -values<sup>48</sup>.

## References

- [1] F. London, *Superfluids. Macroscopic Theory of Superconductivity* (Dover, New York 1961), vol 1.
- [2] N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Holt, Rinehart and Winston, New York 1976).
- [3] J. Bardeen, L. Cooper and J. Schrieffer, *Phys.Rev.***108**, 1175 (1957).
- [4] E. Maxwell, *Phys.Rev.***78**, 477 (1950); C. A. Reynolds et al., *Phys. Rev.***78**, 487 (1950); H. Fröhlich, *Phys.Rev.***79**, 845 (1950).
- [5] G. F. Hardy and J. K. Hulm, *Phys.Rev.***93**, 1004 (1954); B. T. Matthias et al., *Phys.Rev.***95**, 1435 (1954).
- [6] B. T. Matthias et al., *Science* **175**, 1465 (1972).
- [7] Ø. Fischer, *Appl.Phys.***16**, 1 (1978).
- [8] F. Steglich et al., *Phys.Rev.Lett.***43**, 1892 (1979).
- [9] D. Jérôme et al., *J.Phys.Lett.***41**, 397 (1980).
- [10] W. A. Little, *Phys.Rev.***A134**, 1416 (1964).
- [11] V. L. Ginzburg and D. A. Kirzhnits, eds. *High-Temperature Superconductivity*, p.1 (Consultants Bureau, New York 1982); see also *Superconductivity, Superdiamagnetism, Superfluidity*, ed. V. L. Ginzburg (MIR Publishers, Moscow 1987), p. 11.
- [12] J. G. Bednorz and K. A. Müller, *Z.Phys.***B64**, 189 (1986).
- [13] C. W. Chu et al., *Phys.Rev.Lett.***58**, 908 (1987).
- [14] M. François et al., *Solid State Communic.* **63**, 35 (1987).
- [15] P. P. Edwards et al., *Chemistry in Britain* **23**, 962.
- [16] D. Vaknin et al., *Phys.Rev.Lett.***58**, 2802 (1987).
- [17] J. M. Tranquada et al., *Phys.Rev.Lett.***60**, 156 (1988).
- [18] M. Kato et al., *Physica C***152**, 116 (1988).
- [19] P. W. Anderson and Z. Zou, *Phys.Rev.Lett.***60**, 132 (1988).
- [20] C. Ebner and D. Stroud, *Phys.Rev.***B31**, 165 (1985); S. John and T. C. Lubensky, *Phys.Rev.***B34**, 4815 (1986).
- [21] T. A. Falens et al., *Phys.Rev.Lett.***59**, 915 (1987); K. J. Leary et al., *Phys.Rev.Lett.* **59**, 1236 (1987); B. Batlogg, *Proc. Interlaken Conf.*(1988).
- [22] P. Steiner et al., *Z.Phys.***B67**, 449 (1987).
- [23] L. F. Mattheiss, *Phys.Rev.Lett.***58**, 1028 (1987). See also A. J. Freeman et al., *Phys.Rev.Lett.***58**, 1035 (1987).
- [24] D. J. Scalapino et al., *Phys.Rev.Lett.***58**, 1024 (1987).
- [25] B. Szpunar et al., *Physica C***152**, 91 (1988).
- [26] P. W. Anderson, *Science* **235**, 1196 (1987).
- [27] M. Gutzwiller, *Phys.Rev.Lett.***10**, 159 (1963); J. Hubbard, *Proc.Roy.Soc.***A276**, 238 (1963).
- [28] P. Wachter, Conference 6 (Roundtable), in "Superconductivity and Energy", *Science Meeting No.2*, International Science Policy Foundation (European Branch), Lisbon, 21 to 23 March, 1988.
- [29] S. A. Kivelson et al., *Phys.Rev.***B35**, 8865 (1987).
- [30] P. W. Anderson et al., *Phys.Rev.Lett.***58**, 2790 (1987).

- [31] P. B. Wiegmann, Phys.Rev.Lett.60, 821 (1988).
- [32] G. M. Eliashberg, Pisma JETP 46, 94 (1987).
- [33] G. Baskaran et al., Solid State Communic.63, 973 (1987); G. Baskaran, Physica 148B, 200 (1987).
- [34] C. Gros et al., Z.Phys.B68, 425 (1987).
- [35] E. Müller-Hartmann et al., Proc. Interlaken Conf.(1988).
- [36] J. E. Hirsch, Proc. Interlaken Conf.(1988).
- [37] T. Izuyama, J.Phys.Soc.Japan 56, 4247 (1987).
- [38] A. Aharony et al., Phys.Rev.Lett.60, 1330 (1988).
- [39] A. K. Zvezdin and D. I. Khomskii, in "Problems of high  $T_c$  SC, Information Materials", USSR Academy of Sciences (Ural Branch), Sverdlovsk (1987).
- [40] C. P. Enz and Z. M. Galasiewicz, Solid State Communic.66, 49 (1988).
- [41] V. J. Emery, Phys.Rev.Lett.58, 2794 (1987).
- [42] J. E. Hirsch, Phys.Rev.Lett.59, 228 (1987).
- [43] W. Weber et al., Proc.Interlaken Conf.(1988).
- [44] J. R. Schrieffer et al., Phys.Rev.Lett.60, 944 (1988).
- [45] X.-G. Wen and R. Kan, Phys.Rev.B37, 595 (1988).
- [46] C. P. Enz, Proc. Interlaken Conf.(1988).
- [47] R. Oppermann, Proc. Interlaken Conf.(1988) and references therein.
- [48] J. W. Halley and H. B. Shore, Phys.Rev.B37, 525 (1988).