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An Overview of Recent Developments in High-Temperature Superconductivity

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I. BACKGROUND INFORMATION.

SUPERCONDUCTIVITY is a phase, a state of matter (in the sense that ice and steam are phases of water and diamond and graphite are phases of pure carbon) observed in some solids, mostly metals [1-3].

The SUPERCONDUCTING STATE has several characteristic properties:

1.- When it exists for a given substance, it exists only at temperatures below a so-called TRANSITION TEMPERATURE, T_c, and in general down to the absolute zero of the temperature scale ($0\,K = -273.15\,°C$).

2.- It exhibits *d.c.* ZERO RESISTIVITY, i.e. infinite conductivity for zero-frequency measurements (an effect discovered in mercury by Kamerlingh Onnes in 1911).

3.- It exhibits, for weak magnetic fields, perfect DIAMAGNETISM, i.e. its magnetic susceptibility in Gaussian units is given by

$$\chi_M = -(1/4\pi)\,, \tag{1}$$

which means that magnetic flux lines are completely expelled from the superconductor. This effect, known as the MEISSNER EFFECT, was discovered by Meissner in 1933.

4.- There is a minimum energy value -- called an ENERGY GAP [4] -- for exciting the system away from its state of lowest energy (the so-called ground state). This energy gap

$$E_G = 2|\Delta| \ , \tag{2}$$

was conjectured theoretically by London in 1935, deduced from thermodynamic data in 1946, observed by infrared measurements in 1956 and by electron tunneling in 1960.

5.- There is a surprising dependence on the transition temperature, T_c, on the isotopic mass of the atomic nuclei of the superconductor. (It is surprising that a phase which is electric and magnetic in nature, and therefore caused by the *electrons*, depends in any fashion on the mass of the *nuclei*). This is the so-called ISOTOPE EFFECT, was discovered in 1950, and establishes that

$$M^{\alpha} \cdot T_c = constant \ , \tag{3}$$

where M is the nuclear mass and, for various metals, the exponent α takes the values: 0.485 for Pb, 0.415 for Sn, 0.150 for Ti, 0.065for Ru, and -0.015 for Ir.

6.- Superconductivity, in addition to high temperatures, can be destroyed (with a return to the normal state) by either a large enough electric current $I > I_c$, or a large enough magnetic field $H > H_{c2}$. (It should be mentioned that for intermediate field strengths $H_{c1} < H < H_{c2}$, the magnetic flux lines partially penetrate the superconductor but do not destroy the superconducting state). The quantities I_c, H_{c1}, and H_{c2}, are called the CRITICAL CURRENT, and the CRITICAL MAGNETIC FIELDS, respectively.

7.- Superconductivity is a MACROSCOPIC QUANTUM PHENOMENON, with amplitudes and phases associated with the energy gap parameter Δ. Therefore interference and diffraction effects can be achieved, in particular the JOSEPHSON EFFECT [3]. These effects can be fruitfully employed in processing, storing, and retrieving information, i.e. in computer technology.

II. THEORY.

The currently, universally accepted theory of superconductivity, known as the BCS THEORY was formulated [5] by Bardeen, Cooper and Schrieffer in 1957. The theory in its most general form states that, if metallic mobile electrons interact ATTRACTIVELY with each other, then they will condense into a ground state with:

(1) an energy gap in the excitation spectrum;

(2) zero resistivity;

(3) the Meissner effect; and

(4) a phase transition to the normal metallic state at a transition temperature T_c.

There is an important issue to resolve. How can two electrons -- which are charged particles with identical negative charges, and therefore experience a strong Coulomb-force repulsion -- attract one another? The answer is: by polarizing the crystal lattice! [An instructive simile is the attraction that two billiard balls experience when placed on a rubber membrane: one billiard ball falls readily into the depression caused by the other ball, hence it is attracted by the other ball.] Since the polarization of the solid lattice depends on the mass of the nuclei which form it, the strength of the electron attraction depends on the mass of the nuclei, i.e. there is an ISOTOPE EFFECT.

The BCS theory yields, in general, an integral equation for the energy gap parameter Δ, and another integral equation for the transition temperature T_c. These integral equations depend on the electronic structure of the metal, and on the details of the attractive interaction between the electrons. As an example of their theory, Bardeen, Cooper and Schrieffer introduced a very simple model, the so-called BCS MODEL, for which the integral equations can be analytically solved, and that yields

$$\Delta = 1.76kT_c = 2\hbar\omega_D \exp[-1/NV] \ , \tag{4}$$

where k is Boltzmann's constant, ω_D is the vibration (Debye) frequency of the lattice, N is the number of available electronic states per unit energy in the solid (density of states at the Fermi level), and V is the strength of the attractive (lattice mediated) electron-electron interaction.

This simple BCS model gives a good idea of how the BCS theory works: the transition temperature can be increased (1) by increasing ω_D, (2) by increasing N, or (3) by increasing V. [It should be

remarked that the influence of both N and V on T_c is much more dramatic than the simple proportionality of T_c and ω_D.] According to formula (4) there is no maximum transition temperature; T_c can be increased without limit by finding solids with larger and larger N, V, and ω_D.

In fact formula (4) is not accurate: it is only a simple model. A very good an accurate theory, based on the BCS theory, was developed by Eliashberg and McMillan [6] which, given precise experimental information about the solid lattice vibrations, could accurately -- by numerical methods -- calculate the gap parameter Δ and the transition temperature T_c. This theory, with a precision of a few percent, yields excellent results for the transition temperature T_c and the isotope effect exponent α in several well studied cases, mostly transition metals. Numerical experiments performed with the Eliashberg-McMillan equations produced,for sensible input of lattice vibration spectra, superconducting transition temperatures which never exceeded 40 K. Therefore, although no rigorous limit was established for a MAXIMUM SUPERCONDUCTING TRANSITION TEMPERATURE, the belief among most specialists was that such an upper bound existed, and that it was in the range of 30 K to 40 K.

III. HISTORY OF THE HIGHEST SUPERCONDUCTING TRANSITION TEMPERATURES.

The Table below shows the history of the experimentally found highest superconducting transition temperatures:

YEAR	T_c [K]	SUBSTANCE	Notes and References.
1911	4.2	*Hg*	[1]
~ 1913	7.2	*Pb*	
1933	9.5	*Nb*	
1941	16.0	*NbN*	
1953	17.1	V_3Si	
1960	18.05	Nb_3Sn	
1969	20.8	*NbAlGe*	
1973	23.2	Nb_3Ge	[7]
1986	~ 30	*La–Ba–Cu–O*	[8,9]
1986	39	*La–Sr–Cu–O*	[10]
1987	~ 92	*RE–Ba–Cu–O*	*RE* = various rare earths [11,12].
1987	~ 230	*RE–Ba–Cu–O*	not reproducible, unstable! [13]

As can be seen, from 1911 to 1973 the increase in maximum observed transition temperatures was a more-or-less linear function of about 0.3 K per year. No temperature was found to violate the (wrongly believed) upper bound.

For the sake of comparison it should be remembered that liquid helium boils at 4.5 K, liquid hydrogen at 20.7 K, liquid neon at 27.2 K, and liquid nitrogen (i.e. liquid air) at 77.4 K. These are the

most commonly used refrigerants, and any technology based on superconductivity will have its costs determined, almost exclusively, by the refrigeration costs. The discovery of superconducting Nb_3Ge in 1973 was considered a major breakthrough, since for the first time the liquid-hydrogen barrier was crossed. Needless to say the events of the last few months can be considered, by any standards, fantastic: first the liquid-neon barrier was broken; soon thereafter the liquid-air temperature was surpassed; and -- if the elusive and unstable very high temperatures reported recently, but easily lost, are both confirmed and stabilized -- it seems that the dream of room-temperature superconductivity is now within accessible reach.

IV. THE NEW SUPERCONDUCTORS.

The 1987 high-temperature superconductors have a combination of properties which are, except for the HUGE VALUES of the CRITICAL TEMPERATURES, the CRITICAL MAGNETIC FIELDS, and the ENERGY GAPS, not really unusual. They are all four- or five-component COPPER OXIDES. They are poor conductors in the normal state. They have a very LOW CRITICAL CURRENT. They exhibit, to a varying degree, an ISOTOPE EFFECT. The various substances exhibit a rich variety of solid-state phases. Some of the phases are ANTIFERROMAGNETIC. Some of the phases are INSULATING. The superconducting phases are VERY ANISOTROPIC, with characteristics which make them look either as layered compounds (i.e. with strong two-dimensional features), or, in some cases, as linear chains (i.e. with one-dimensional characteristics). They are all incredibly easy to manufacture (which makes one wonder why were they not discovered before). They are also difficult to produce in a single phase, and even more difficult to produce as single crystals (all known single crystals are, as far as the author is aware, twins). But the main fact is that they are, in all respects, traditional superconductors: they exhibit all the features (1) through (7) discussed in Section I.

Theories, speculations, and explanations for these fascinating substances abound. In fact the 1987 Physics, Chemistry, and Materials Sciences literature has been flooded with papers aiming at either partial or comprehensive elucidation of the superconducting behavior of these oxides. Needless to say, the "theories" are mostly divergent, and clash with one another. As more experimental

facts become known and detailed data become available most, if not all, will be discarded. A critical discussion of the merits and drawbacks of the various attempts is, at this point, a rather futile exercise. It is important, however, to underline some of the ideas currently being pursued, and the main features of these theories/speculations:

1.- The new superconductors are layered solids, and this anisotropy may be the dominant feature which produces the high transition temperatures. (There are many other layered superconductors, e.g. $NbSe_2$ either pure or intercalated with other substances, including organic molecules. These "two-dimensional" superconductors have "ordinary" transition temperatures, in the range 5 K to 15 K).

2.- The lattice vibrations of these oxides may be unusually soft, with a consequent enhancement of the superconductivity. (This is a common feature of many other superconductors, and leads to high, but "ordinary" transition temperatures, easily explained by the Eliashberg-McMillan equations).

3.- The magnetism -- especially the antiferromagnetism -- of these substances may play an unusual and crucial role. (Although antiferromagnetism and superconductivity are known to coexist in some cases, e.g. $ErRh_4B_4$, magnetic moments, and especially ferromagnetic arrangements, tend to destroy, not enhance, superconductivity).

4.- These substances are oxides, and the oxygen ion must play a crucial role in the superconductivity. (There are other oxide superconductors, e.g. $LiTi_2O_4$ with a transition temperature of 13.7 K, discovered in 1973, and $BaPb_{1-x}Bi_xO_3$ with a transition temperature of 13 K, discovered in 1975, but they are the exception rather than the rule).

5.- The electrons may be in these substances very tightly bound in pairs and behave like the atoms of superfluid helium. (This is the so-called "Bose condensation of bipolarons"; most experimental evidence seems to be against this type of explanation).

6.- The repulsion between the electrons caused by the Coulomb forces, coupled to their motion in the solid lattice, must produce a repulsion at short distances, but could produce an attraction at intermediate distances which may lead to a superconducting state. (It should be noted that the Coulomb repulsive interaction normally hinders rather than favors the appearance of a superconducting state. In fact the Coulomb repulsion, coupled to quantum-mechanical effects, is

responsible for the appearance of the various forms of magnetic ordering, including ferromagnetism and antiferromagnetism).

7.- The lattice vibrations do not play (or at most play a minor) role in the superconducting properties of these oxides. (This will be a completely new feature for superconductors: all other superconductors are known to be a consequence of the electron-electron attractive interaction caused by a lattice polarization. An explanation of this sort could take care of the violation of the Eliashberg-McMillan upper bound, but will contradict the observation of the isotope effect in these high transition temperature superconductors).

8.- The BCS theory should be discarded for these substances and a new state of matter, with radically different properties should be postulated. (Unfortunately this type of explanation seems to be doomed to failure, since these are, except for the large values of the parameters, ordinary superconductors in all respects. And it should be remembered that the BCS theory is not only one of the most successful physical theories ever formulated, it has great predictive values: in all cases its predictions have been confirmed -- over and over again -- by experiment).

V. CONCLUSIONS.

The BCS theory, in all probability, will explain the properties of these new superconducting materials. However, a detailed account of why they have such an unusually high transition temperature will require much more work, mostly careful, well designed, well executed experiments.

The key to the answer to the theoretical questions may be found in the fact that all these materials are ceramics, i.e. BAD CONDUCTORS in their normal phase. In fact, they are "ALMOST INSULATORS", with strange and varied MAGNETIC PROPERTIES. And although the lattice polarization will certainly play a role (as shown by the isotope effect), the detailed motion of the electrons and the short-range Coulomb repulsion may give the unusual characteristics which result in high transition temperatures.

From the point view of practical applications and their implications in our everyday life, much can be speculated: transmission lines without any power losses, levitated trains, super-supercomputers, new and not-yet-invented devices. But all these innovations will require the solution of

complicated (and expensive to solve) materials problems (brittle, hard to handle ceramics; unstable phases; low critical currents) as well as a cool-headed economic analysis which this author is unable to provide.

But, from the point of view of the scientific and technological challenge, the fun has just begun. Hard work lies ahead, but is challenging, exciting work, with potentially enormous rewards.

FOOTNOTES AND REFERENCES

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