Superconductors with Superconducting Transition Temperatures $T_c = 91\text{K} (1999)$, $120\text{K} (1994)$, $340\text{K} (2000)$, and $371\text{K} (1995)$: Experimental Errors or a Technological Puzzle? Two-Component Nonstoichiometric Compounds and the Insulator–Superconductor–Metal Transition.

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One of the reasons for the lack of understanding of both the mechanisms underlying the HTSC phenomenon and of the instability of materials with $T_c > 300\text{K}$ may be the widely accepted but wrong ideas about the types of chemical bonding in a substance and the radii of the atoms and ions. A revision of these concepts started in the beginning of the XX century in connection with the investigation of nonstoichiometric compounds (the berthollides) but did not reach a critical level until recently. Most of the HTSC materials, however, are actually two-component nonstoichiometric nanocomposites (the berthollides), whose components "dilute" or "stretch" one another. Each component resides in an "intermediate" state, which still remains poorly studied. For instance, in a system of particles having two paired electrons each (divalent particles), the unbroken electron pairs may start tunneling at a certain "medium" concentration (or in the temperature interval $T_1 < T < T_2$) with the system becoming a Bose superconductor (the state between the insulator and the metal with BCS superconductivity). For univalent atoms (Na, Ag), however, such possibility realizes neither in the intermediate (the Mott transition) nor in the final state. Univalent metals are not superconductors. In the berthollides, however, a possible Jahn–Teller–Peierls-type instability may give rise to formation of diatomic molecules (Na$_2$, Ag$_2$) with electron pairs, and superconductivity can set in. It is possibly such systems that were obtained by chance in experiments with univalent components and reported to have $T_c$ of up to 371K. Structures of a number of HTSC materials are considered.

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In the recent decade, several reports from independent sources announced synthesis of substances with the superconducting transition occurring at $91\text{K}$ [1], $120\text{K}$ [2], $340\text{K}$ [3], and $371\text{K}$ [4]. These experiments, however, neither have received confirmation nor were continued. In all the cases, the reason for this was the poor reproducibility of the synthesis and the instability of the samples. It is this feature, however, that is the main structural characteristic of HTSC substances with the model of superconductivity used to interpret the metallization of xenon under pressure [5] and, later, applied to two-component nonstoichiometric compounds with incommensurate parameters of the constituents (matrix systems) [6]. In addition to the instability common to all the four substances, they have also certain common physical features characteristic of the given superconductor model, which permits one to consider their appearance not as due to experimental errors but rather as chance occurrences of technological nature associated with structural instabilities.

Synthesis of superconductors with $T_c > 300\text{K}$ and elucidation of the mechanisms underlying high-temperature superconductivity are issues that are still awaiting solution. One of the reasons for this may be the widely accepted but inadequate concepts concerning the part played by the atomic and ionic states (and by their radii) in the structure of a substance. A revision of these concepts started in the beginning of the XX century in connection with the investigation of nonstoichiometric compounds (berthollides). The lack of understanding of their nature has not, however, reached a critical level until recently. Indeed, we may recall that most of the HTSC compounds are actually berthollides, and their physical properties cannot be understood properly without a correct description of their chemical structure. Rather than being uniform chemical substances, the berthollides can be, for instance, two-component nonstoichiometric nanocomposites, with each of the components "diluting" or "stretching" the other. They stabilize one another in an unusual, "intermediate" state, which remains poorly studied. If, for instance, particles having two paired electrons each (divalent particles) approach one another, a real state may form within a narrow interval of concentrations (or temperatures) between the insulator and the metal, a state where pair tunneling has already started, and where, while their binding energy has already begun to decrease, the electron pairs have not yet split into fermions (as is the case with the final, metallic, equilibrium state for $T > T_2$). The system

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transfers to the state of a Bose condensate. A Bose superconductor forms between the insulator and the metal with BCS superconductivity within a narrow and structurally unstable region. For univalent atoms (Na, Ag), however, such possibility realizes neither in the intermediate (the Mott transition) nor in the final state. Univalent metals are not superconductors. In the berthollides, however, a possible Jahn–Teller–Peierls-type instability may give rise to formation of diatomic molecules (Na$_2$, Ag$_2$) with electron pairs and superconductivity can set in. It is possibly such systems that were obtained by chance in experiments with univalent components and reported to have $T_c$ of up to 371K. In the berthollides, stability is a consequence primarily of their architecture rather than of chemical interactions, a point that is frequently disregarded, thus bringing about a distorted picture of physical phenomena. This may come from a wrong determination of the type of chemical bonding in the given structure because of the use of wrong values of the radii and charges of the particles, a possibility substantiated by a comparison of experimental data with quantum-mechanical calculations of the radii of atoms and, particularly, of ions. For instance, the radius of the O$^{2-}$ ion is not 1.4Å but 0.6Å, and that of Cu$^{2+}$, 0.33Å rather than 0.73Å.

Two-component nonstoichiometric compounds are relatively inert matrices with voids of diameter $D$ containing not ions but atoms, whose diameters $d$ are slightly larger than those of the free atoms but smaller than of atoms in a metal. When atoms are removed from the metals (or when the number of the nearest neighbors decreases), their diameter decreases by only 10% — 15% (the Goldschmidt contraction). Each component is a stoichiometric substance, whose structure may be not necessarily stable in itself. While atoms of metals, for instance, can have close-to-metallic radii, the component itself may turn out to be an unusual, "stretched" or "dilute" metal, and not a Fermi substance, whose structure may be not necessarily stable in itself. While atoms of metals, for instance, can have close-to-metallic radii, the component itself may turn out to be an unusual, "stretched" or "dilute" metal, and not a Fermi substance, whose structure may be not necessarily stable in itself. 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(1) The case of $D \sim (3 - 10)d$. Belonging here are, for instance, the zeolites with substances embedded in the structural voids. The clusters in the voids are domains of the second phase. The system as a whole may be treated also as a "supercrystal".

(2) The case of $D \leq d$. Atoms of the second component (but not ions) stretch the matrix. This case, well known in chemistry, relates directly to the nonstoichiometric compounds (the berthollides or interstitial compounds). It can be illustrated by the MeB$_6$ system. A sublattice of the metal atoms rather than of the matrix-doping ions is inserted into the voids of the framework between the B$_6$ octahedra. This is indicated by the framework stretching, with $d$, the diameter of the atom, exceeding $D$, which is the MeB$_6$ lattice parameter. For Me = Ce, La, Ca, Sr, Ba the ratio $D/d$ is Ce (4.14/3.26), La (4.15/3.74), Ca (4.15/3.95), Sr (4.19/4.30), and Ba (4.27/4.34). The sublattices of Ce, La, and Ca are stretched, and those of Sr and Ba compressed, but at the same time the B$_6$ framework is stretched. Metal ions could not stretch the framework. All these compounds feature about the same melting points $T \sim 2200$K, which are determined by the rigid covalent B$_6$ framework.

(3) If $D \geq d$, the case of perovskite-like structures, the atoms of the second Me component inserted in the voids of the matrix $Mt$ can undergo a 3D Jahn–Teller–Peierls transition with formation of diatomic molecules made up of atoms which occupy neighboring voids. After all the voids have filled (Me$_1$Mt$_1$), one can conceive of the following possibilities:

(A) formation of regular structures of diatomic molecules;

(B) formation of disordered structures.

In both cases, a matrix-stabilized second phase will appear. This phase is at the same time "diluted" by the matrix.

If not all of the voids are filled (a technological problem), the composition of the substance can be written as $Me_xMt_1$ for $x < 1$, which likewise suggests two possibilities:

(a) - domains with all voids filled will form (a version of cases A and B);

(b) - a component with a low concentration of diatomic molecules forms.

Realization of version (b) is a still more complex technological problem, but it is such systems with very high $T_c$ that were apparently obtained accidentally.

I. If the inserted atoms are univalent, the diatomic molecules will have two paired electrons and a binding energy $E_m = E_0(d-D)/d$, where $E_0$ is the binding energy of the Me metal. As the concentration $N$ of such molecules increases, or the temperature decreases, the thermal de Broglie wavelengths $\lambda_{dB} \sim T^{-1/2}$ of the electron pairs and the mean intermolecular distances $N^{-1/3}$ may become comparable. It gives rise to Bose-Einstein condensation at $\lambda_{dB}^3 N > 2.612$. The condensation phenomenon of the Bose-Einstein statistics is distorted, of course, by the presence of molecular forses and by fact that it manifests itself not in the gaseous state. But the same problems exist in the case of liquid helium as well. The system will transfer from the insulator to the Bose superconductor state with the transition temperature $kT_{cn} = kT_B = 3.31(h/2\pi)^2N^{2/3}/M = 1.04(h/2\pi)^2n^{2/3}/m$, where $n = 2N$ and $m = M/2$ are the electron concentration and mass, respectively. For $T_B = (15, 70, 325)$K, we obtain $n = (2 \times 10^{18}, 2 \times 10^{19}, 2 \times 10^{20})$ cm$^{-3}$. The transition temperature can, however, be governed by the $E_m$ energy as well, as is the case with metals ($T_{cm}$). As the temperature increases to $kT > kT_{cm} \sim E_m$, or the concentration rises to $n > n_{crit}$ (ultimately to $x = 1$), the bosons will separate into the fermions, and the system will become Fermi type with the temperature $T_F > T_B$. Therefore, such systems can become superconducting only within a narrow region of concentrations of atoms (molecules) or temperatures ($T_1 < T_c < T_2$). These are either doped semiconductors,
or "stretched" or "diluted" metals; being actually real systems, they are not Fermi type but rather unstable, and it is such systems that are dealt with here. Such systems can become superconducting not only through formation of electron pairs (\(T_{cm}\)) as is the case with metals, but as a result of Bose condensation of the bosons present in the system (\(T_{cm} = T_B\)). An increase in the concentration of \(Me\) atoms drives the insulator–superconductor–metal transition.

II. If two paired electrons, rather than belonging to molecules, are outer electrons of a divalent atom, for instance, of Mg, the components need not necessarily be incommensurate. One has only to produce in the voids of an inert matrix a local concentration of the metal atoms \(Me_x\) within a certain interval \(x < 1\) (provided there are no domains with \(x = 1\), as is the case with an equilibrium Fermi metal). The mechanism of preservation of electron pairs in metals, if they form for \(T < T_{cm}\) from the outset as superconductors, is described by BCS theory (the Cooper pairs).

Univalent metals do not have such "relic" states, and this is what accounts for their not exhibiting superconductivity.

Compression of a metal usually reduces \(T_c\). Hence, Cooper pairs in a "stretched" metal are bound stronger. They are much closer to the state of atomic electron pairs.

\[\text{MgB}_2\]. It is a version of such a "diluted metal" that possibly is realized in the \(\text{MgB}_2\) system. The divalent magnesium is "diluted" by boron layers in the form of a covalently bonded hexagonal network. The \(\text{MgB}_2\) lattice parameters are \(c = 3.40\,\text{Å}\), \(a = 3.05\,\text{Å}\). Each B atom has three nearest neighbors. The B–B distance, 1.77 Å, is larger than the dimensions of the atom, 1.55 Å, than that in the B2 molecule (1.59 Å), and that in \(\text{MeB}_6\) (1.72 Å), which has five nearest neighbors. Having a nearly covalent diameter (3.08 Å), the magnesium atoms stretch the boron atom network. This produces conditions favorable for the formation of \(\text{B}_2\) molecules. The Mg atoms confined between the B layers are also slightly stretched along the c axis as compared to their diameters in the metal (3.20 Å). This system revealed two energy gaps proportional to \(T_{cm1} = 15\,\text{K}\) and \(T_{cm2} = 45\,\text{K}\).

\[\text{Me}_3\text{CoO}_2\] Another illustration of superconductors with a stretched component (version \(D \lesssim d\)) is provided by the \(\text{Me}_3\text{CoO}_2\) fullerides. Their \(T_c = T_{cm} \sim E_0(D - D_0)/D_0\), where \(E_0\) is the binding energy of the \(\text{CoO}_2\) spheres, \(D_0\) is the fullere lattice parameter, and \(D\) is this parameter increased by incorporation of \(\text{Me}_3\) clusters into the octahedral voids \(\mathbb{R}\). \(T_{max} \approx 40\,\text{K}\).

\[\text{Na}_x\text{CoO}_2 - 1.3\text{H}_2\text{O}\]. The superconductivity \((T_c \sim 4\,\text{K})\) observed in the \(\text{Na}_x\text{CoO}_2 - 1.3\text{H}_2\text{O}\) system is due to the univalent sodium, possibly as a result of formation of weakly bound Na\(_2\) molecules. The optimum concentration of Na is \(x = 0.3\) \(\mathbb{R}\), i.e., it is "intermediate", as in many other cases. It is stabilized by the \(\text{H}_2\text{O}\) molecules (an "additional diluent" or third component).

\[\text{Na}_x\text{-NH}_3\]. The same molecules (Na\(_2\)) formed undoubtedly in the \(\text{Na}_x\text{-NH}_3\) solutions as well \((T_c \sim 200\,\text{K})\). The instability of this system originates from fast phase separation in the liquid, and the decrease in the solution density can be traced to the increase of the atomic volume of sodium in diatomic molecules and the interphase "gap" \(\mathbb{R}\) rather than to the formation of "bubbles" \(\mathbb{R}\).

\[\text{Y}_2\text{Ba}_4\text{Cu}_6\text{O}_{14}\]. The well studied system \(\text{Y}_2\text{Ba}_4\text{Cu}_6\text{O}_{14}\) (85K) \(\mathbb{R}\) can also be treated in terms of the above scheme. Its lattice parameters are \(c = 11.681\,\text{Å} = 3 \times (3.894)\,\text{Å}\), \(a = 3.886\,\text{Å}\), \(b = 3.827\,\text{Å}\). This structure may be considered also as a slightly distorted simple cubic lattice of spheres with an average diameter of 3.86 Å. It corresponds to the average diameter of the Y and Ba atoms in these spheres of 3.87 Å. The diameters of the free atoms are 3.38 Å and 4.12 Å, and those of the ions \(\text{Y}^{2+}\) and \(\text{Ba}^{2+}\), 1.28 Å and 1.73 Å. The diameters of the atoms in the metal are 3.56 Å and 4.34 Å. The density of this lattice is 0.52 ("dilute metal"). The remainder of the volume, 0.48, is taken up by the \(\text{Cu}-\text{O}\) octahedra and pyramids and the interphase "gap" \(\mathbb{R}\). Each oxygen atom is also bonded covalently to six or eight nearest oxygen atoms. Sulfur, an analog of oxygen, also exhibits a tendency to formation of structures of a molecular type (\(\text{S}_2\), \(\text{S}_6\), \(\text{S}_8\)). In the case of oxygen, this process requires a "seed" (Cu) for its realization. The Cu\(_3\text{O}_7\) component is a stoichiometric compound with O–O covalent bonding. It is stable naturally only in the framework of the Y-Ba2 lattice. Both components stabilize one another. The Y and Ba sublattices are "diluted," and the Y sublattice, "stretched" as well (\(\text{Y}_2\)). Hence, the volume of the Cu\(_3\text{O}_7\) component is not governed by the ion diameters, either traditionally accepted (1.46 Å and 2.8 Å) or calculated (0.65 Å and 1.20 Å) \(\mathbb{R}\).

\[\text{Na}_0.05\text{WO}_3\]. The properties of two-component nonstoichiometric compounds become most clearly pronounced in the \(\text{Me}_2\text{WO}_3\) tungsten bronzes \(\mathbb{R}\). The bronze with an average composition \(\text{Na}_{0.05}\text{WO}_3\) was found to be superconducting with \(T_c = 91\,\text{K}\) and to have an energy gap \(E \sim 160\,\text{K}\). The substance is unstable. The parameter \(D = 3.78\,\text{Å}\). In the Na metal, \(d = 3.72\,\text{Å}\). In this case, for \(E_0 = 1\,\text{eV}\) in sodium we obtain for the gap energy \(E_m = E_0(D-d)/d = 0.016\,\text{eV}\), which implies that the transition is energy driven. Free Na\(_2\) molecules have a binding energy of 0.35 eV. In the \(\text{WO}_3\) matrix, their energy is 20 times smaller (0.35/0.016) . Their detection is made difficult by the fact that the modulation of the period is only 0.016 . \(\text{WO}_3\) is a standard stoichiometric compound (\(\text{W}^{6+} - \text{O}^{2-}\)). However, in this compound each oxygen atom has likewise eight nearest oxygen atoms. Therefore, its physico-chemical bonding is also a quantum-mechanical superposition of several types of states \(\mathbb{R}\). Remarkably, replacement of Na by Rb or Cs, for which \(D < d\), lowers sharply \(T_c\) (from 91K down to \(-3\,\text{K}\)). Substitution of Na by Li or Ag (\(d \sim 3.10\,\text{Å}\)) was not tried, because Na, Rb, and Cs were considered as dopants only (i.e., in the ion form), rather than a second
component in a nonstoichiometric compound.  

Ag–Y–Ba–Cu–O. Substitution of this type was made earlier in the Y–Ba–Cu–O system. One doped it with silver, which raised $T_c$ to 120K.  

Ag$_2$Pb$_2$CO$_9$. The use of silver in the Ag$_2$Pb$_2$CO$_9$ system also brought about an increase in $T_c$ to 340K. The "colossal electrical conductivity $>10^8$ Ohm$^{-1}$cm$^{-1}$" observed to occur in the Ag$_2$Pb$_2$O$_6$ system between 210K and 525K is assigned to a heating-induced segregation of the Ag component in channels of the Ag$_3$Pb$_2$O$_6$ lattice. The composition proposed for this compound is $\text{Ag}_2\text{Ag}_3\text{Pb}_2\text{O}_6$. If this state is indeed superconductivity, it becomes realized within the interval ($T_1 < T_c < T_2$) (i.e., under heating).

$\text{YBa}_2\text{Cu}_3\text{Se}_7. T_c$ can be increased not only by reducing $d$ but by increasing $D$ as well. The oxygen in the standard Y–Ba–Cu–O system was replaced by selenium, which brought about an increase in the lattice parameter, after which $\text{YBa}_2\text{Cu}_3\text{Se}_7$ exhibited $T_c \sim 371$K.  

One can conceive also of a specific class of two-component nanocomposites of a "dynamic" type. These are condensates of molecular, or noble gases. In these condensates, a certain number of virtual excimer molecules, for instance, Xe$_2^*$, with two paired electrons, are present in the lattice of Xe atoms residing in the ground state ("matrix"). It is supposed, that increasing the Xe$_2^*$ concentration either by applying pressure or through the action of catalysts (atoms of metals) could give rise to Bose superconductivity with high $T_c$. The investigation of the Mott transition in metal–inert-gas nanocomposites and of adsorption forces (sorption compounds) is dealt with in a large number of publications (see, e.g., [21, 22, 23, 24]). It is quite possible that a W–Ar sorption compound forms in the gas sheath surrounding the tungsten filament in the course of metal vaporization in conventional gas-filled tubes. Metallization of this layer brings about a drop in the voltage across the filament with increasing current [25]. One cannot exclude here, however, the possibility that the increase in the conductivity of the gas is actually the result of its ionization.  

Thus, the major technological difficulty in the way of developing HTSC materials consists in preparing stable systems of particles with paired electrons (for instance, divalent atoms or molecules) in concentrations at which the electron pairs already are capable of tunneling (Bose condensation) while not yet separating into single electrons, either as a result of conventional chemical interactions or through a decrease in their binding energy in an effective dielectric medium. Such an intermediate state corresponds to a "stretched" or "diluted" substance, which can be stabilized by using "solid solvents" as matrices. The highest $T_c$ were obtained with univalent metals (not superconductors), because their diatomic molecules can exist in the matrices in low enough concentrations. In some cases such nonequilibrium concentrations are possibly "frozen" by chance fluctuations in the technology of synthesis [1, 2, 3, 4]. Stability has thus far been reached apparently at the expense of a low $T_c$. In searching for efficient methods of structural stabilization, (with help of some amount of inert particles as "additional diluent" (third component), for instance) a better understanding of the quantum-mechanical interactions in the structure of each component is of crucial importance. Such methods of stabilization can be found only by using realistic atomic and ionic radii rather than conventional quantities, which are nothing else but a consequence of postulated bonding types. The matrices in such nanocomposites also exist in an unusual state because of the unusual structure and contact interaction with the second component. This complicates greatly the investigation and description of such systems.

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