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The chemical and adsorption effects of foreign molecules on the properties of high-temperature superconductors

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Abstract. Data on the effect of adsorption and intercalation of foreign molecules on the properties of high-temperature superconducting materials and on the reciprocal effect of superconductivity on the electronic state of adsorbed molecules are considered. Particular attention is given to the analysis of experimental conditions and interpretation of the results obtained. An effect of adsorbed molecules on the electrophysical state and the critical parameters of superconductors is noted. Specific features of the interaction between the phases in the superconducting state and the external molecules are discussed. The bibliography includes 280 references.

I. Introduction

The discovery of oxide materials which become superconductors at the liquid nitrogen temperature[1,2] has resulted in a rapid development of studies of their physicochemical properties. These studies showed that the high-temperature superconductivity (HTSC) is extremely sensitive to the effect of the environment.

An opinion exists that superconductors are thermodynamically unstable systems.[3] On the other hand, it was shown in one of the first reviews on the thermodynamic properties and stability of yttrium-containing superconducting ceramics[4] that, although the $YBa_2Cu_3O_7$ phase is somewhat unstable thermodynamically, it can exist almost infinitely in this state. As a result of interaction of oxide ceramics with foreign molecules, superconductivity can both disappear and appear. Both of these phenomena have been observed experimentally in a study of the effect of the external molecules on the properties of HTSC oxides. Systematic analysis of the effect of foreign molecules on HTSC materials can help to reveal new ways for reaching high superconducting transition temperatures.

From the applied viewpoint, an important task is to obtain HTSC materials with high critical superconductivity parameters, *viz*., temperature (T_c), current (I_c) and current density (J_c). Research on both classical low-temperature superconductors and HTSC materials has shown that high critical currents can be obtained if the superconductor structure incorporates an optimum number of defects acting as pinning centres for the Abrikosov vortices. Systematic studies of processes for the controlled formation of defects in superconducting materials has led to the conclusion that the intercalation of various chemical admixtures produces additional pinning centres, and hence increases the critical current density.

Recently, great interest arose in new electronic sensors which contain layers of organic molecules or polymeric films deposited on the surfaces of semiconductors or metals.[5–7] Such elements have a significant advantage over the usual inorganic solid-state sensors, *i.e*., enhanced sensitivity and selectivity with respect to environment.[8–10] A novel class of oxide materials, *viz*., high-temperature superconductors that possess a combination of unique physical properties at relatively high temperatures, has also become the subject of intense studies aimed at their application in similar electronic elements. For instance, it was found that molecular dye layers deposited on a Josephson junction made of superconductors increase considerably the sensitivities and selectivities of light sensors with respect to visible light.[11–13] This was the first documented example of the effect of the properties of an HTSC material on the electron state of adsorbed organic molecules.

In this review, we have analysed the reported data on the effect of adsorption and intercalation of molecules on the physicochemical properties of ceramic and film HTSC materials and on the effect of the superconducting state on the low-temperature adsorption, catalysis and the electronic state of the molecules adsorbed on the HTSC material surfaces. Intensive studies are now being carried out along these lines, hence our review cannot claim to be comprehensive. In some cases, the interpretation of certain experimental results can be debatable. Nevertheless, the possibility of the reciprocal influence of the superconducting state and the molecular processes on the surface of HTSC materials is an established fact, which however requires detailed studies.

II. Some specific features of the physicochemical properties of high-temperature superconductors

All high-temperature superconductors are copper-containing oxides of complex chemical composition. As a rule, each unit cell of an HTSC phase incorporates from four to six chemical elements.[14]

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The data from small angle neutron scattering indicate that polycrystalline HTSC materials contain rather branched systems of pores connected to the surfaces of samples.[15] Hence, molecules from the environment can readily penetrate into the specimen and react with the superconducting phase. The specific surface of such specimens measured by the Brunauer–Emmett–Teller (BET) method on the basis of the low-temperature nitrogen adsorption is from 0.2 to 1.5 $m^2\ g^{-1}$, which is rather high for compact ceramic materials. The thermodynamic instabilities of HTSC materials can manifest themselves in their smaller stabilities in comparison with those of simpler low-temperature superconductors, *viz*., metals and alloys.

Obviously, the effect of foreign molecules on HTSC materials can be rather complex. In addition, the study of these effects and particularly their interpretation can be complicated considerably because the surface chemical composition of an HTSC material differs significantly from its bulk composition.

In order to classify possible mechanisms of the interaction between the HTSC materials and the external molecules, it is worthwhile to consider some characteristic features of the structure of these materials and the mechanism of the initiation of the superconducting state.

1. Specific features of the structure of high-temperature superconducting oxides

Such multi-component oxide systems as La–Ba(Sr)–Cu–O, Y–Ba–Cu–O, Bi–Sr–Ca–Cu–O with perovskite-like or defective perovskite-like structures (Fig. 1) represent typical HTSC materials.[16, 17]

Virtually all HTSC materials are characterised by the existence of copper–oxygen layers and chains. The first and most important factor enabling superconductivity to appear is the existence of at least two types of copper coordination in the structural cell of the material; this results from the ability of the lattice copper ions to exist in several oxidation states, namely Cu(I), Cu(II) and Cu(III). Overlapping of the 3*d* orbitals of copper with the 2*p* orbital of oxygen results in the formation of a valence band and strong delocalisation of the holes.[18] In the structure of CuO_2 (the copper–oxygen layers), the holes migrate along the oxygen anions, which makes the $3d^9$L-type electron configuration much more probable than $3d^{10}$L (where L is the oxygen vacancy).[19] This specific behaviour of copper ions (in particular, the possibility of existence in several different coordinations) is closely related to a manifestation of the Jahn–Teller effect by these ions.

The second factor responsible for the superconductivity of oxide systems is the low spatial dimensionality of the electronic structure, which is nearly two-dimensional. The low effective dimensionality of the electronic structure of HTSC materials results from the presence of the copper–oxygen layers (see Fig. 1). It is in these layers that the electrons providing the superconductivity are localised. The low structural dimensionality of an HTSC material is directly proved by strong anisotropy of superconductivity: the critical current along the crystallographic axes *a* and *b* is by an order of magnitude higher than that along the *c* axis.[20, 21]

The low dimensionality of the electronic structure is not the only factor which enables the possibility of existence of the superconducting state. For example, it has been shown[22] that the superconductivity of La_2CuO_4 is much more strongly affected by violation of the stoichiometry of this oxide with respect to oxygen than by structural changes. The non-stoichiometry effect becomes more pronounced as the La : Cu atomic ratio decreases. The excess of copper favours the formation of additional oxygen vacancies; this facilitates the incorporation of oxygen during synthesis, resulting in partial oxidation of Cu^{2+} into Cu^{3+}. Unlike $La_{2-x}Cu^{II}O_4$, the $La_{2-x}Cu^{II/III}O_4$ compound is a superconductor.

In $YBa_2Cu_3O_{7-x}$, violation of stoichiometry occurs due to the filling of the oxygen rows at the O(4) position (see Fig. 1 *b*).[23–25] The superconducting orthorhombic structure of $YBa_2Cu_3O_{7-x}$ exists at the oxygen index $x \leqslant 0.6$. For $x > 0.6$, the unit cell of this oxide is characterised by a non-superconducting tetragonal structure. Figure 2 shows the dependence of the superconducting transition temperature on the oxygen index *x*.[24] One can see that the quantity of the excess (or mobile) oxygen affects substantially the ceramics superconductivity.

The role of oxygen in HTSC materials has been discussed in several publications (see, *e.g*., Refs 23, 24, 26–28). In the orthorhombic phase of $YBa_2Cu_3O_{7-x}$, oxygen can occupy different crystallographic positions:[27] the O(2) and O(3) positions in the $[CuO_2]$ plane and two positions, O(1) and O(4), in the Cu–O chains (see Fig. 1 *b*). The oxygen states O^{2-}, O^- and O_2^{2-}, which exist in dynamic equilibrium and affect the superconducting and chemical properties of the majority of HTSC materials, have been predicted theoretically and found experimentally.[28] The high oxygen mobility in the material bulk is provided by the oxygen

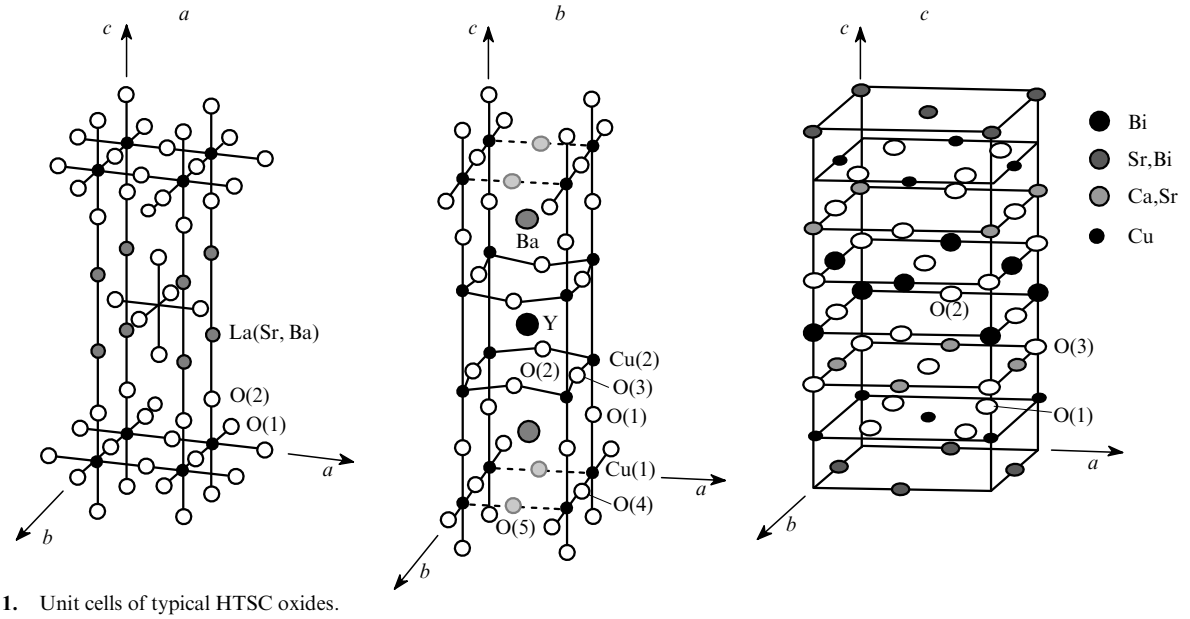


Figure 1. Unit cells of typical HTSC oxides.
(*a*), $La_{2-x}Sr_x(Ba_x)CuO_4$; (*b*), $YBa_2Cu_3O_{7-x}$; (*c*), $Bi_2(Ca,Sr)_3Cu_2O_z$ (one half of the unit cell is shown).[16, 17]

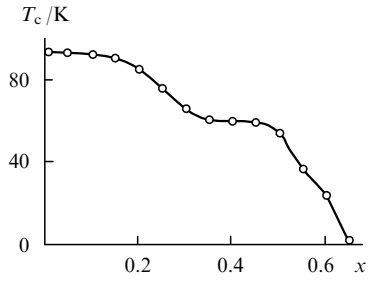


Figure 2. Dependence of T_c of the $YBa_2Cu_3O_{7-x}$ ceramic on the oxygen index x.[24]

forms which have the smallest charge or even no charge at all, whereas electron migration is provided by the O^{2-} ions.

2. Structures of polycrystalline specimens

Ceramic polycrystalline HTSC materials are of the greatest interest. This is due to their accessibility and relative simplicity of their preparation, which enables the synthesis of single-phase specimens with high superconducting transition temperatures. The main obstacles to the wide practical application of polycrystalline superconductors include the low critical currents and their rapid decrease as the field increases. In addition, ceramic HTSC materials have low corrosion resistance.

A polycrystalline HTSC material (ceramic) is a system of anisotropic superconducting granules with sizes ranging from 1 to 100 μm; they are linked in a three-dimensional network of weak Josephson junctions.[27,28] In a general case, a sandwich-like structure of the SNISN type appears on the boundaries between the granules (where S is a superconductor; N is a layer with normal metallic conductivity or a superconductor layer with a lower critical temperature; I is a dielectric or semiconductor layer). The thickness of the boundary layer allowing superconductivity current to flow between the granules should not exceed the coherence length along the crystallographic axis c [$\varepsilon_c(0\ \mathrm{K}) = 0.2$ nm] and in the ab plane [$\varepsilon_{ab}(0\ \mathrm{K}) = 1.64$ nm].[29]

Weak bonds between the granules of ceramic HTSC materials differ in nature. In this review, we shall consider only those typical features of the structure and properties of inter-granule layers that can be affected by molecules foreign to the given material, namely: (1) non-stoichiometry of granules with respect to oxygen in the near-boundary layers; (2) high probability of admixture segregation at the inter-granule boundaries; (3) possibility of defective packing; (4) presence of 'foreign' or amorphous phases at the inter-granule boundaries.

The oxygen non-stoichiometry is due to surface rearrangement because of a decrease in the surface energy at the granule boundaries. The boundary layers with a high fraction of the lattice sites belonging to both contacting microcrystals are also energetically favourable.

Studies of admixture-free boundary granule layers of single-phase ceramic with composition $YBa_2Cu_3O_{7-x}$ (Refs 30–33) showed that enrichment of granules with copper and their depletion of oxygen occurs in a boundary layer no thicker than 5 nm. The phase formed at the granule boundaries has a orthorhombic structure.

Within the percolation theory based on the random distribution of oxygen defects, the critical oxygen deficiency (the oxygen index x) was determined; above this value, the oxygen-enriched structures (superconducting granules) are separated with insulating layers and the inter-granule superconductivity transport current is absent.[34] The value of x for the $YBa_2Cu_3O_{7-x}$ HTSC ceramic found by the Monte Carlo method for a square lattice (two-dimensional superconductivity) was 0.26.[34]

Segregation of admixture atoms and phases at granule boundaries seems to be the simplest and most natural reason for the formation of inter-granular layers possessing metallic conductivity and/or dielectric properties. In most cases, carbon and/or carbon-containing compounds constitute one of the main admixtures on the granule surfaces. Carbon can originate not only from the starting compounds used for the material synthesis, *e.g.*, barium carbonate, but also from atmospheric carbon dioxide.[35–37] If excess $BaCO_3$ is present in the starting mixture for the ceramics synthesis, carbon is segregated on the granule boundaries and forms a coating 1–4 monolayers thick.[38] It is of note that carbon is not present on intergranule fractures.

In addition to carbon and its compounds, non-superconducting phases formed from the starting compounds due to incomplete synthesis were found on granule boundaries.[39,40] For example, local melting at granule boundaries in copper–barium–yttrium HTSC materials at synthesis temperatures above 930 °C results in the formation of regions enriched with barium (the $BaCuO_2$ phase), yttrium (the BaY_2CuO_5 phase) or copper (the liquid phase).[41]

The formation of defective packing in the crystal structure at inter-granule boundaries and the formation of a twinning structure in the ceramic microcrystals are accompanied by relaxation of elastic stresses that appear upon structural phase transitions in the temperature range from 873 to 973 K. For example, the absolute majority of the granule boundaries of the $YBa_2Cu_3O_{7-x}$ ceramics contain inter-layers consisting of blocks of atomic planes $CuO_2-BaO-(CuO_2)-BaO_x$ *ca.* 1.5 nm thick; this is explained by the breaking of the layered structure in $YBa_2Cu_3O_{7-x}$. This process is similar to the formation of the $YBa_2Cu_4O_{7-x}$ phase with a critical temperature of 80 K.[42–44] Since the coherence length along the axis c is 0.7 nm, the presence of such inter-layers on the boundaries of the majority of granules should have a strong adverse effect on the ability of the ceramics to conduct electric current.

The presence of the twinning structure inside the microcrystalline granules favours the formation of domains shaped as long (up to 1 nm) narrow 'bands' parallel to the (110) or $(1\bar{1}0)$ axes. The width of these domains varies from 5 to 300 nm and depends on the technique for the ceramic's synthesis and on the granule size.[45] These structures also deteriorate the current-carrying ability of HTSC materials.

3. Properties and structures of real high-temperature superconducting oxide surfaces

The interaction of the external molecules with an HTSC material starts at its surface. It has been noted above that, generally, the chemical composition, state, and structure at the surface and in the bulk of a superconductor differ considerably. However, the properties of the surface layer of an HTSC material affect directly the electronic properties and superconductivity parameters of the bulk phase.[46]

The surfaces of the specimens are highly non-uniform. They contain macroscopic defects, such as growth steps, cracks, pores, dislocation exits, *etc*. Due to the interaction of coordination- and/or valence-unsaturated surface atoms with the external molecules, various chemical components are invariably present at the surface.

The adsorption of molecules and atoms often changes the properties of the surface itself, particularly the electron state of the surface atoms. The study of the $YBa_2Cu_3O_{7-x}$ ceramic by photoemission spectroscopy revealed a difference in the state of the 'pure' and 'contaminated' surfaces.[47] Typical contaminations appear due to the chemisorption of the H_2O, CO, and CO_2 molecules. The content of surface carbonates on 'contaminated' specimens is 10 at.%–15 at.%, while that on a 'pure' specimen is 1 at.%. The surface also contains barium hydroxide, copper oxides, various yttrium compounds and the so-called 'green' phase, *i.e.*, Y_2BaCuO_5. The surface copper exists in the Cu^+ and Cu^{2+} states;[48] the near-surface layer does not possess superconductivity.[49] It is therefore obvious that controlled surface cleaning is an important problem in studies on the effect of the surface states on the material superconductivity.

It is well known that chemical etching of polycrystalline films of $YBa_2Cu_3O_{7-x}$ with solutions of halogens and hydrogen halides in alcohols improves the stoichiometric composition of the surface and decreases considerably its contamination with carbonates and hydroxides.[50] For example, it was shown [51] that the electric characteristics of the tunnel contact between the $YBa_2Cu_3O_{7-x}$ film and metallic niobium are improved considerably after chemical etching of the film. In this case, an inter-layer of the SNS type is formed in which the surface resistance is almost 30 times smaller and the critical current is 40 times greater than those in contact *via* a non-cleaned surface. An inter-layer between the superconductors can be fabricated by chemical etching. Probably, this type of treatment of superconducting ceramics not only decreases considerably the surface contamination but also brings about certain chemical modification of the surface layer of the $YBa_2Cu_3O_{7-x}$ system due to reactions of halogens and hydrogen halides with metal oxides on the surface. In fact, treatment of an $YBa_2Cu_3O_{7-x}$ film surface with a 1%–2% solution of Br_2 or HBr in ethanol results in the following surface compounds: YBr_3, $BaBr_2$ and CuBr.[52] Scanning electron microscopy did not reveal any significant changes in the surface morphology after chemical etching. It is important that surface treatment of this type increases its resistance against atmospheric gases.

Interesting results were obtained by bombardment of HTSC film surfaces with argon and oxygen ions. Bombardment with argon ions with an energy of 500 eV results in strong damage of the surface layer.[23, 53] Oxygen atoms are preferentially removed from the surface and hence copper is reduced (while electroneutrality is maintained). This damage affects directly the oxygen vacancies and causes disordering of the near-surface layer atoms. As a result, the superconductivity characteristics of the films become much worse. However, the original properties of the films are completely restored after annealing in pure oxygen.

Quite a different picture is observed if the surface of an HTSC material is bombarded with oxygen ions.[54] In this case the surface etching rate is higher than that in the case of argon bombardment. After a brief bombardment, the dependence of the superconducting transition temperature for the $YBa_2Cu_3O_{7-x}$ film on the etching time passes through a maximum with $\Delta T = 2$ K and then tends to the original value.

Hence, cleansing of the surface of an HTSC material by bombardment with oxygen ions is preferable to cleansing with argon ions. The mechanism of the effect of high-energy oxygen ions on the superconductivity transition temperature is not quite clear yet. However, it can be assumed that during bombardment with O^- ions, the surface layer, which is originally depleted of oxygen, is forcedly saturated with it, which favours the formation of the superconducting phase.

Although scribing (mechanical surface cleaning) of the $YBa_2Cu_3O_{7-x}$ ceramic decreases the contamination with foreign molecules, it damages the surface considerably.[55] Studies of the surface by characteristic electron energy loss reflection spectroscopy showed that the near-surface layer contains an excess of barium and oxygen atoms, while the surface concentration of the copper–oxygen planes is insignificant. This is explained by the fact that scribing mostly results in microcrystal breaking along the inter-granule boundaries or at the Ba–O planes. In addition, preferential diffusion of the Ba–O complexes over the surface occurs.

One should pay attention to the nature and structure of the adsorption-active sites capable of adsorbing foreign molecules on the surfaces of HTSC materials. As shown in earlier studies,[56] the structures of real surfaces of oxide semiconductors and dielectrics are rather complex. The nature of the adsorption-active sites is determined by the state of oxygen in the near-surface region: deficiency or excess of oxygen give rise to electron-donating or electron-withdrawing active sites, respectively.

Studies of the $YBa_2Cu_3O_{7-x}$ ceramic surface revealed active sites consisting of Cu^+ cations and an oxygen vacancy ($\square$, hole), which is an electron acceptor.[57] At room temperature, an active site of the [Cu^+, $\square$] type is stabilised by the elastic strain field of dislocations or by boundaries of twinning structures.[58] At 400 K, diffusion of the interstitial O^- ions begins to the sinks on the surface (holes or dislocation exits). Trapping of the O^- ion by the oxygen vacancy results in electrically neutral oxygen and a free electron. A fraction of the O^- ions reaching the Cu^{2+} surface ions can transfer a hole to them; this probably results in Cu^{3+}. Subsequent evolution of the active site at 580 K involves migration of neutral oxygen from the bulk; it 'catalyses' the decay of the [$2Cu^{3+}$, $2O^{2-}$] site accompanied by the emission of the O^{2-} and Cu^{2+} ions to the surface.[59] The disappearance of the O_2^{2-} bipolarons (local hole pairs) after the first heating *in vacuo* at 623 K makes the transition of this ceramic to the superconducting state at $T > 77.4$ K impossible.

The evolution of the state of oxygen on the $YBa_2Cu_3O_{7-x}$ surface at low temperatures was studied [59] by recording the transformation of the O(1*s*) X-ray photoemission spectrum upon temperature decrease from 300 to 110 K. At 110 K, the O^- ions in the near-surface region are dimerised to give the O_2^{2-} dimer, but the oxidation state of the copper ions remains unchanged. Simultaneously, the surface electric conductivity increases.

III. The effects of adsorption and intercalation of simple compounds on the properties of high-temperature superconductors

Intercalation of simple molecules into HTSC ceramics is accompanied by various physicochemical transformations: replacement of nodal atoms in the crystal lattice, intrusion of foreign molecules into the interstitial space, diffusion of molecules along the ceramic granule boundaries and formation of strong chemical bonds at the surface.

Unfortunately, the available experimental data do not allow yet an unambiguous conclusion regarding the nature of the interaction between small molecules and the superconductor material to be made.

For example, it is believed that the low-temperature adsorption of molecules on oxides is generally of physical character, hence it is non-specific and its dependence on the availability of adsorption sites and the electron state of the surface is insignificant. Physical adsorption can result in only small changes in the surface charge and the vibration modes of the surface atoms. However, in reality the adsorption of certain molecules on HTSC materials at $T < 300$ K affects their superconductivity; this cannot be explained by simple physical adsorption. As a rule, the changes in the superconductivity characteristics observed in these cases are related to intercalation or inclusion phenomena of molecules into the structure. The possibility of intercalation and chemical interaction of simple gases with HTSC materials at high temperatures (> 473 K) has been established reliably and does not raise doubts (see below).

1. The effect of oxygen

Oxygen plays a particularly important role in the formation of the structure of perovskite-like complex oxide materials and in their transition to the superconducting state. In addition, the oxygen molecule is a paramagnetic species, its adsorption on a superconductor surface can affect directly the superconducting properties. The techniques for obtaining HTSC materials and the role of oxygen in the formation of superconducting phases have been well covered in the literature. The reaction pathways of oxygen with HTSC materials during the synthesis and high-temperature treatment are so diverse that, despite a great number of publications, this phenomenon still remains insufficiently studied because the problem of non-stoichiometry with respect to oxygen and the related phenomena for the $RBa_3Cu_3O_z + O_2$ systems (where R is a rare-earth element) are excessively complex.[60] We shall only discuss the main aspects of such interactions.

One of the first Russian reviews devoted to the role of oxygen in HTSC materials was published in 1989.[61]. In the final stage of the synthesis, the oxide $YBa_2Cu_3O_{7-x}$ is saturated with oxygen. When compact ceramics are being obtained, this process is rather complicated, particularly in the synthesis of highly oxidised specimens ($x \to 0$). It was shown in a study of the oxidation kinetics of ceramic specimens of various densities at 773 K that slow oxygen absorption by compact ceramics results from transition of the reaction from the diffusion mode to the kinetic mode due to accumulation of considerable elastic strain in the material.[62] Thermodynamic estimates showed that the elastic strain energy upon oxygen absorption by compact ceramics can affect the oxidation kinetics only in the case where the base planes contain oxygen ions of two types, namely, those strongly and weakly bound to the lattice.

The diffusion of oxygen into the $YBa_2Cu_3O_{7-x}$ ceramic was described [63] within a one-dimensional diffusion model. The equations obtained provide a good description of the experimental results on the oxygen exchange kinetics. The transformation of the specimens during oxygen diffusion in the temperature range of 423–973 K and at oxygen pressures of 1.4–10.7 atm involves three stages. A solid solution of oxygen in the tetragonal phase $YBa_2Cu_3O_6$ is formed in the first stage.[64] In this case, the diffusion factor is described by an Arrhenius dependence with the activation energy of 0.14 eV, while the pre-exponential factor depends on the oxygen pressure. In the second stage, oxygen starts to diffuse along unordered CuO chains in the tetragonal phase. The diffusion factor is also described by an Arrhenius dependence, but the activation energy is 0.6 eV and the pre-exponential factor no longer depends on the oxygen pressure. In the third (final) stage where the tetragonal phase is transformed to the orthorhombic one the diffusion factor becomes smaller than that in the tetragonal phase and gradually decreases to zero as the transition to the ideal orthorhombic phase of $YBa_2Cu_3O_{7-x}$ occurs.

Subsequent systematic studies of oxygen desorption from the $YBa_2Cu_3O_{7-x}$ ceramic at high temperatures showed [65, 66] that this process probably occurs according to a different mechanism. The main features of this process will be described in more detail below; for now, let us note that the adsorption of molecular oxygen on the surface of an HTSC material occurs according to the dissociation mechanism, whereas desorption occurs according to the association mechanism. The oxygen atoms occupy the vacant positions, *i.e.*, O(1) or O(5), in the near-surface layer of the crystal lattice. The exchange and transport of oxygen during the adsorption–desorption processes on the $YBa_2Cu_3O_{7-x}$ ceramic probably involves oxygen vacancies according to the relay-race mechanism.

The kinetics of oxygen evolution from the $YBa_2Cu_3O_{6.92-x}$ ceramic with $x < 0.54$ was studied in the temperature range of 600–950 K using the thermo-programmed desorption method.[65] At $T < T_m$ (where T_m is the temperature corresponding to the desorption peak maximum), the desorption rate is described fairly well by a second-order kinetic equation which is formally consistent with associative desorption. Oxygen-deficient specimens with $x < 0.25$ are characterised by a noticeable increase in the activation energy accompanied by an increase in the pre-exponential factor; this implies the presence of a compensation effect.

Many authors (see, *e.g.*, Refs 26, 67–69) consider the surface potential barrier as the main obstacle to the release of oxygen from HTSC materials. It was shown convincingly that the nature of this barrier is determined by the surface energy parameters.[69] For example, the oxygen desorption rate increased, whereas the desorption activation energy decreased by 0.2±0.03 eV after vapour phase deposition of several monolayers of silver on the surface of a sample of $YBa_2Cu_3O_{7-x}$ ceramic. Changes in the surface properties should not affect the oxygen desorption rate if oxygen diffusion in the granules is the limiting step of this process. UV photoelectron spectroscopy data suggest that the electron work function for the yttrium ceramic's surface decreases by 0.3 eV upon vapour deposition of silver. It is thought that this decreases the surface energy barrier.[69] The results of this experiment also indicate that the barrier is in fact energy-related rather than resulting from the formation of a particular surface structure. The temperature where oxygen starts to enter the ceramic was observed to decrease upon 'mild' treatment of the ceramic with molecular hydrogen.[70, 71] This is also evidence of the importance of surface barriers. The temperature of oxygen penetration into HTSC ceramics also decreased upon thermal vacuum treatment [72] and after plasma treatment.[73]

Several parameters characterising the surface potential barrier for the release of oxygen atoms were determined.[74] It was found by isotope exchange between the gas phase and the surface of a $YBa_2Cu_3O_{7-x}$ single crystal under the conditions of isochronous and isothermal annealing of the specimens that the activation energy for oxygen desorption is 1.08 eV. In the authors' opinion, this indicates that the sorption mechanism of the formation of the surface barrier upon isotope exchange is somewhat preferable. However, an unambiguous conclusion on the surface barrier nature could not be made within the scope of this study. The use of polycrystalline specimens instead of single crystals does not affect the main results.

Degradation of HTSC materials at room temperature in the presence of water vapour is accompanied by the loss of oxygen from the HTSC phase. The water layer adsorbed on the superconductor surface probably favours the acceleration of oxygen exchange between the HTSC material and the gaseous environment.[75, 76] It was confirmed [75] that oxygen is desorbed at room temperature from the $YBa_2Cu_3O_{7-x}$ ceramic covered with an adsorbed water layer. In this case, the basic orthorhombic phase O_I is coated with a modified orthorhombic O_{II} phase with $T_c = 60$ K. The proportion of the O_{II} phase increases with an increase in the degree of hydration of the material and decreases upon annealing the specimen at 913 K.

The low-temperature oxygen exchange between the $YBa_2Cu_3O_{7-x}$ ceramic and the gas phase is limited by the surface potential barrier. Probably, the adsorbed layer of water molecules lowers this barrier significantly. On the other hand, it was shown theoretically [77] that the diffusion of O^{n-} oxygen ions inside the crystal lattice 'channels' [1/2, *b*, 0], which can be regarded as the oxygen sublattice, occurs without activation and does not limit the redox processes. The hypothesis on the high mobility of oxygen in the $YBa_2Cu_3O_{7-x}$ lattice at low temperatures was confirmed.[76] It should be noted that the high mobility can also involve a different mechanism. Based on thermogravimetric and X-ray diffraction analyses and electric conductivity measurements, a scheme for $YBa_2Cu_3O_{7-x}$ reduction at room temperature was suggested. According to this scheme, the oxygen diffusion is considered as an activationless process. Depending on the water vapour pressure, the stage limiting the oxygen exchange rate also changes. The oxygen exchange between $YBa_2Cu_3O_{7-x}$ and the gas phase at $p_{H_2O} \geqslant 760$ Pa is limited due to the presence of a chemisorbed water surface barrier. In the pressure range $250 < p_{H_2O} < 760$ Pa, the rate of $YBa_2Cu_3O_{7-x}$ reduction is limited by the step of O^{n-} anion diffusion through the layer of physically adsorbed H_2O molecules, while at $80 < p_{H_2O} < 250$ Pa, the movement of the O^{n-} anions is hindered by the twinning boundaries. At the lowest humidities ($p_{H_2O} < 80$ Pa), all the above factors no longer operate, and the reduction rate exceeds 0.15 mass % min^{-1}. However, a layer of the tetragonal phase is formed after some time on the $YBa_2Cu_3O_{7-x}$ surface; this layer does not conduct oxygen ions at low temperatures.

A study [66] of the oxygen isotope exchange between ^{18}O from the gas phase and ^{16}O from the $YBa_2Cu_3O_{6.92}$ ceramic in the temperature range of 293–923 K aimed at the elucidation of the nature of labile oxygen, which plays an important role in heterogeneous oxidation. The maximum oxygen isotope substitution at 923 K was 3.8±0.3 a.u. per formula unit of the cuprate. It was assumed that the chain [O(4)] and bridging [O(1)] oxygen atoms in the cuprate crystal lattice are replaced almost completely. Hence, it is in these positions that labile oxygen, which probably partic-

ipates in catalytic oxidation on the surface of these ceramics at $T > 800$ K, is localised.

The inequality of the oxygen atom positions in the CuO_2 and *ab* planes results from the orthorhombic structure of the $YBa_2Cu_3O_{7-x}$ crystal. According to the experimental data [78–81] and theoretical calculations,[82] the activation energies $E_a^{O(3)}$ and $E_a^{O(2)}$ for oxygen exchange between the O(3) and O(2) positions (see Fig. 1 *b*) are equal to 1.02 eV and 1.18 eV, respectively. The transition from the O(3) to the O(2) position occurs with an activation energy of

$$E_a^{O(3)} = E_0 - \Delta E,$$

and the transition from the O(2) to the O(3) position occurs with an activation energy of

$$E_a^{O(2)} = E_0 + \Delta E.$$

The difference between these energies, $2\Delta E = 0.16$ eV, is explained by the unequal O(3) and O(2) oxygen positions in the orthorhombic lattice, where the oxygen–copper bond along the *a* axis is longer than that along the *b* axis. To the first approximation, the ratio of the occupancies of these positions with oxygen is described by the Boltzmann equation

$$\frac{N_0^{O(3)}}{N_0^{O(2)}} = \exp\left(-\frac{2\Delta E}{kT}\right),$$

while the oxygen index is described by the expression

$$x = N_0^{O(3)} + N_0^{O(2)} - 1.$$

The features of oxygen ordering in $YBa_2Cu_3O_{7-x}$ ($x \approx 0.1$) were studied by transmittance electron spectroscopy and electron microdiffraction.[83] Near the superconducting transition point, oxygen ordering occurs in the $YBa_2Cu_3O_{7-x}$ crystal; this is accompanied by an increase in the orthorhombic parameter

$$R = \frac{|a-b|}{a+b}.$$

These results suggest that oxygen atoms can diffuse in the crystal even at liquid nitrogen temperature.

Based on elastic relaxation measurements in the $YBa_2Cu_3O_{7-x}$ ceramic in the temperature range of 283–1073 K, the activation energy of oxygen exchange between the O(4) and O(5) positions (see Fig. 1 *b*)

$$E_a = 1.07 \text{ eV}$$

and the pre-exponential factor in the Arrhenius equation for the self-diffusion factor

$$D_0 = 1.8 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$$

were found for various oxygen partial pressures.[78] The activation energy decreases with an increase in the oxygen content in the ceramics. More detailed data on E_a and D_0 can be found elsewhere.[60]

The phase stability of copper cuprates is directly related to the diffusion of labile oxygen. A novel technique based on direct coulometric titration was developed for the study of the redox kinetics of $YBa_2Cu_3O_{7-x}$ and for the measurement of the oxygen diffusion factor under various conditions.[84] It was found experimentally that the oxygen diffusion factor in the specimens decreased monotonically with a decrease in x from 0.8 to 0.1. In the authors' opinion, this phenomenon can be explained by the vacancy-related oxygen diffusion mechanism. The temperature dependences of the measured diffusion factors obey the Arrhenius equation; these are in good agreement with previous results (see, *e.g.*, the review [26]). In continuation of these studies,[85] the phase stability limits of the compounds $RBa_2Cu_3O_{7-x}$ (R = Y, Nd) were determined over a broad range of oxygen partial pressures. For R = Nd, the stability limit lies at higher temperatures than for R = Y. This is explained by a decrease in the energy of repulsion between the oxygen ions due to the larger distance between them because of the larger ionic radius of Nd^{3+}. The dependences of the diffusion parameters (D_0, E_a) on the oxygen non-stoichiometry index (x) and on the oxygen partial pressure were found. The diffusion of oxygen in the orthorhombic phase occurs faster than in the tetragonal phase. Practical recommendations were given for reducing the probability of microcrack formation, improving the contacts between the crystallites and shortening the low-temperature annealing when the HTSC ceramics are oxidised in the final stage of synthesis.

Studies on oxidation of the $YBa_2Cu_3O_{7-x}$ ceramic under polythermal conditions showed that the temperature dependence of oxidation obeys the Arrhenius function, while the activation energy of this process changes monotonically as x increases.[86] In the ranges $0.2 < x < 0.3$ and $0.6 < x < 0.7$, the $E_a(x)$ dependence displays characteristic breaks. The authors suggest that this is closely related to a change in the mechanism of oxygen ion ordering in the CuO_z planes. In the first case, a change in the oxidation mechanism results from the fact that 1/9 of the oxygen vacancies residing in the planar planes are occupied and their subsequent chaotic occupation is no longer possible. The second break most probably corresponds to the transformation of the tetragonal phase to the orthorhombic phase.

The diffusion of oxygen in $Y_{1-y}Pr_yBa_2Cu_3O_{7-x}$ was studied [87] by measuring the electric conductivity of a sample in the temperature range of 300–1000 K. The desorption of oxygen from $Y_{1-y}Pr_yBa_2Cu_3O_{7-x}$ was much slower than that from the pure $YBa_2Cu_3O_{7-x}$ phase and decreased with an increase in y. The number of charge carriers in the ceramics studied was controlled by the oxygen content and did not depend on the Pr concentration.

The specific features of the thermal destruction of HTSC materials were analysed.[88] Analytical expressions for the dependence of the extent of oxygen non-stoichiometry on temperature and pressure were suggested on the basis of pseudo-chemical reaction models with consideration of the formation of point defects on copper ions and oxygen vacancies. It was found that the thermal destruction kinetics of high-temperature superconductors are described by chain nucleation equations.

A study of the processes of oxygen evolution from the $YBa_2Cu_3O_{7-x}$ ceramic upon thermal desorption *in vacuo* (10^{-5} Pa) revealed three characteristic temperature regions of oxygen evolution with maxima at 517, 673 and 932 K.[89] The first region corresponds to the loss of the chemisorbed, weakly bound oxygen; the second region, to the transformation of the ceramic from the orthorhombic phase to the tetragonal phase involving cleavage of the O–Cu(III) bonds; the third region, to the decomposition of this phase to give yttrium and barium cuprates as well as copper oxides with cleavage of the O–Cu(II) bonds. Thermogravimetric analysis of the $YBa_2Cu_3O_{7-x}$ ceramic *in vacuo* at temperatures up to 1273 K revealed two temperature regions (673–873 and 1173–1233 K) where mass loss occurred due to the loss of oxygen.[90] The first region corresponds to the reversible oxygen loss related to a change in the copper oxidation state, $Cu^{2+} \rightarrow Cu^{+}$, whereas the second region corresponds to the irreversible oxygen loss accompanied by the destruction of the perovskite structure of the ceramics and formation of barium and yttrium cuprates.

Annealing of the $YBa_2Cu_3O_{7-x}$ ceramic *in vacuo* at 10^{-3} Pa and 1073 K results in the destruction of the orthorhombic structure.[91] On average, up to two oxygen atoms are removed from each unit cell, and the ceramic acquires a composition described by the formula $YBa_2Cu_3O_6$. Oxygen is completely removed from the O(4) positions (one atom per cell) and partially from other positions (see Fig. 1 *b*). The oxidation state of one-third of all copper ions becomes equal to unity. Annealing of the sample in air at 773 K results in the intercalation of oxygen into the material crystal structure; the overall number of oxygen atoms per unit cell reaches six.

The isothermal oxidation of the $YBa_2Cu_3O_{7-x}$ ceramic comprises two stages, *viz.*, a diffusion-controlled stage and a 'slow' one

where the oxide is in equilibrium with the gas phase. The stepwise increase in the parameter x over time during the 'slow' stage was studied.[92,93] This stepwise change in x is due to the structural transformation of the tetragonal phase to the orthorhombic one; as a result, mechanical stress is generated in the crystal, which is followed by its relaxation. This effect is described fairly well within the framework of a model which takes not only the T and p_{O_2} parameters but also the elastic intercrystallite interaction energy into account. The kinetics of oxidation of the $YBa_2Cu_3O_{7-x}$ ceramic in the temperature range of 748–873 K was explained[94] using a concept according to which the oxygen diffusion in the tetragonal cuprate phase occurs at the O(4) and O(5) vacancies and is thermally activated, while in the orthorhombic phase it occurs along specific structure 'channels' and does not require thermal activation. The oxygen migration in the orthorhombic phase is controlled by the interaction of the oxidant with the domain boundaries.

A study of the thermal stability of the orthorhombic phase of $YBa_2Cu_3O_{7-x}$ *in vacuo* and in oxygen showed that transformation of the orthorhombic phase to the tetragonal phase *in vacuo* (10^{-3} Pa) occurs at 973 K.[95] An increase in the oxygen pressure to 1 Pa increases the transformation temperature to 1073 K, while in pure oxygen, at a pressure of 10^5 Pa, this value is as high as 1173 K. A phase diagram that characterises the dependence of the temperature of transformation of the orthorhombic phase to the tetragonal phase on the oxygen pressure has been published.[96]

Diffusion processes in thin superconducting films differ from those in bulk ceramic materials and single crystals. The diffusion of oxygen in thin epitaxial films of $GdBa_2Cu_3O_{7-x}$ was studied by measuring the electric resistance under isobaric and isothermal conditions in the temperature range of 650–1050 K.[97] Fast oxygen diffusion occurs preferentially at defects located along the c axis and with low activation energies. Chemical diffusion at vacancies occurs in the *ab* plane. The diffusion factor D in films thicker than 10 nm is $\sim 10^{-13}$ cm^2 s^{-1}. The thermal activation of diffusion is well described by an Arrhenius-type dependence and does not depend on the film thickness. At oxygen pressures around 10^2 Pa, the activation energy is 1.5 eV. However, if the film is thinner than 10 nm, the oxygen diffusion along the c axis is hindered due to the effect of the intermediate layer at the superconducting film–support interface.

It is important to establish the mechanism of the oxygen effect on the superconductivity parameters because it is necessary to solve the problem of the nature of the superconducting state.

Methods for the determination of the ΔH°_{298}, S°_{298}, and C°_{p298} values and for the evaluation of the upper temperature threshold of superconducting transition of Y–Ba–Cu–O HTSC systems were developed with the use of thermodynamic simulation.[98] The oxygen content decreases abruptly in the temperature range of 200–500 K in complete agreement with the temperature dependences of Cu^{3+} concentration in the solutions studied. The Cu^{3+} concentration (at.%) as a function of the x index is described by linear equations for all solutions in the range of 100–900 K. For example, the equation for $YBa_2Cu_3O_z$ is

$$[Cu^{3+}] = -433.866 + 66.71538z\,, \qquad (1)$$

where $z \geqslant 6.5$.

Direct comparison of the resulting Cu^{3+} concentrations with the z values for real superconductors is incorrect, since the structures of a superconductor and a model solution should be different, in accordance with the calculation conditions. However, the authors give certain recommendations regarding the applicability of the results obtained to the study of real superconductors. An equation was suggested for the superconducting Y–Ba–Cu–O system relating the Cu^{3+} concentration to the superconducting transition temperature (in K):

$$T_c = 45.32265 + 1.4333[Cu^{3+}]\,. \qquad (2)$$

The inaccuracy of T_c calculation using Eqn (2) is considerable, since the phases obtained are usually thermodynamically unstable under the conditions of synthesis. The correlation Eqns (1) and (2) can apparently be useful for rough estimates of T_c if the z index is known.

The application of the Langmuir–Maclin model made it possible to determine more accurately the oxygen diffusion factors in $YBa_2Cu_3O_{7-x}$ powdered superconducting ceramics at various temperatures.[99] The overestimated values for powders with particle sizes of 100 μm were explained by the existence of 'easy pathways' for diffusion such as cracks, grain boundaries, *etc*., the role of which is particularly great for particles larger than separate superconductor crystallites.

A study of the physicochemical nature of oxygen dissolution and ordering of oxygen vacancies determining the superconducting properties of the $YBa_2Cu_3O_{7-x}$ ceramic[100] showed that an oxygen solution in the ceramic is somewhat comparable with an ideal gas (*i.e*., obeys the Fermi–Dirac distribution), which is an important disagreement with the widespread concept of the 'regular' character of solid solution. The authors believe that the ordering of oxygen vacancies in the $YBa_2Cu_3O_{7-x}$ ceramic, which provides high-temperature superconductivity, results from structure transformations according to a mechanism related to the Jahn–Teller effect rather than from the interaction (repulsion) between the dissolved oxygen atoms.

The evolution of oxygen from the $YBa_2Cu_3O_{7-x}$, $La_{2-y}Ba_yCuO_x$, $Bi_4Ca_3Sr_3Cu_4O_x$, $Bi_{2-y}Pb_yCa_2Ba_2Cu_3O_x$ and $Tl_2Ca_2Ba_2Cu_3O_x$ ceramics *in vacuo* (10^{-4} Pa) with heating of the specimens to 1173 K was studied.[101] At 773–923 K, oxygen evolution from the yttrium and thallium ceramics was observed. Oxygen was not evolved from the bismuth and lanthanum ceramics in the temperature range studied. According to the published data,[89] the evolution of oxygen from the $Bi_2Sr_2CaCu_2O_x$ system *in vacuo* occurs only in the temperature range of 1223–1323 K.

Thermogravimetric analysis showed[102] that the $Bi_2Sr_2Ca_2Cu_4O_x$ ceramic contains over-stoichiometric oxygen: a specimen prepared in an oxygen atmosphere has the composition $Bi_2Sr_2Ca_2Cu_4O_{11.38}$. The existence of the excess oxygen is explained by the presence of copper ions in a high oxidation state (Cu^{3+}). This observation was also confirmed in other studies.[103–105]

A considerable increase in the superconductor transition temperature of the $Bi_2Sr_2CaCu_2O_{8+x}$ ceramic was observed after it was annealed in oxygen.[106] Raman spectroscopy studies showed that oxygen is included in the Bi–O layers and the increase in T_c is due to the oxygen exchange between the Bi–O and Cu–O layers (see Fig. 1 *c*).

The authors of the present review studied the effect of low-temperature (77.4–100 K) adsorption of O_2, Ar and N_2 on the superconductivity of a $GdBa_2Cu_3O_{7-x}$ thin film.[107] All experiments were conducted *in situ* in an adsorption reactor placed in the probe of a magnetic susceptibility measuring device. The temperature dependence of the real and imaginary parts of magnetic susceptibility, $\chi'(T)$ and $\chi''(T)$, were recorded after the next gas portion was injected into the reactor at 77 K. All of the gases mentioned above affected the shape of the $\chi'(T)$ curve in the vicinity of T_c and 'shifted' the maximum of the $\chi''(T)$ curve towards the low-temperature region. The half-width of the $\chi''(T)$ peak decreased with an increase in the quantity of injected argon and nitrogen and increased upon injection of oxygen; this meant an increase and decrease in the critical currents in the superconducting film with an increase in the degree of its coverage with the gas molecules. The effects of the gases were reversible: removal of the adsorbed molecules by evacuation or by purging with helium at room temperature resulted in complete restoration of the original shapes of the $\chi'(T)$ and $\chi''(T)$ curves.

Comparison of experimental $\chi''(T)$ curves[107] with results of theoretical calculations for the hysteresis losses in thin superconductors[108,109] afforded critical current densities extrapolated to 0 K, $J_c(0)$, and their dependence on the degree of surface coverage with adsorbed gas molecules (Fig. 3). The adsorption of

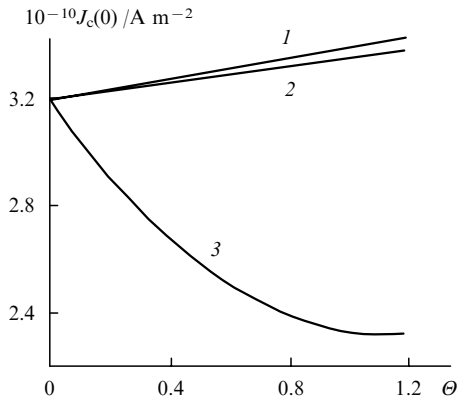


Figure 3. Dependence of J_c extrapolated to 0 K on the degree of coverage of the $GdBa_2Cu_3O_{7-x}$ film surface with N_2 (*1*), Ar (*2*) and O_2 (*3*) molecules.[107]

argon and nitrogen is accompanied by a small increase in $J_c(0)$, whereas the adsorption of oxygen decreases this parameter. On the other hand, the superconducting transition temperature did not vary with an increase in the degree of surface coverage; only 'blurring' of this transition in the vicinity of T_c increased.

The decrease in the critical current density in the case of low-temperature oxygen adsorption is due to the effect of the paramagnetic O_2 molecule on the transport characteristics of the intergranular layers. In fact, the magnetic field strength at a distance from the adsorption site of an oxygen molecule equal to the diameter of this molecule is ~ 10 T. This field strength is quite sufficient for a total perturbation of superconductivity of the intergranular layers. The rather small decrease in the critical current density observed probably results from the fact that the distances of the adsorption sites of the oxygen molecules from the superconducting phase exceeds substantially the molecule size, *e.g.*, due to the presence of a 'buffer' non-superconducting oxide layer on the film surface.

The 'blurring' of the superconducting transition due to the low-temperature adsorption of oxygen, argon or nitrogen can be caused by many reasons. A most likely reason involves inclusion of the molecules of these gases directly into the crystal lattice of the material. This hypothesis was suggested long ago (see below) and was partially confirmed experimentally for argon adsorption.[110] It is likely that the inclusion of simple molecules into polycrystalline HTSC oxides at low temperatures is facilitated by the presence of numerous defects and oxygen vacancies in the crystal lattices of these materials. For instance, the high surface defectiveness is indicated by experimental results of a study of electron photoemission from the $YBa_2Cu_3O_{7-x}$ surface [111] which showed that if the ceramic is crushed, the lattice oxygen leaves the surface instantly even at the liquid nitrogen temperature.

Similar changes in the superconductivity characteristics were recorded for the low-temperature adsorption of oxygen on the $YBa_2Cu_3O_{7-x}$ ceramic.[112] At 77.4 K, this adsorption results in a strong decrease in the transport critical current. The amplitude of the changes was much greater than that in the case of a superconducting film; this is probably due to the presence of a large number of weak bonds between the granules.

2. The effect of hydrogen

The specifics of the interaction of hydrogen with metal oxide superconductors primarily result from the presence of the O^{2-} and O^- ions and possibly O^0 in the anion sublattice; hydrogen readily forms chemical bonds with these species to give OH^- ions or water molecules.[113] Hydrogen that has penetrated into the crystal lattice of an HTSC material reacts with the metal ions to change their effective oxidation state. All of these changes affect, directly or indirectly, the hole concentration in the CuO_2 plane, and hence, the superconducting transition temperature.

The neutron diffraction method was used to study hydrogen adsorption on the $YBa_2Cu_3O_{7-x}$ ceramic in the temperature range from 333 to 593 K.[114] At low temperatures, hydrogen is preferentially adsorbed on the granule boundaries, but above 493 K, it undergoes chemical reactions with the superconductor material. Hydrogen adsorption at elevated temperatures results in partial amorphisation of $YBa_2Cu_3O_{7-x}$ accompanied by the evolution of a considerable amount of metallic copper. According to the reported data,[115] treatment of the $YBa_2Cu_3O_{7-x}$ ceramic with hydrogen at 393–473 K results in a strong decrease in the low-field magnetic susceptibility and suppression of magnetic hysteresis at high fields. The superconducting transition temperature is not changed in this case. The suppression of the magnetic properties of the HTSC material is explained by the formation of metal hydrides in the inter-granular layers; the invariance of T_c is explained by the stable superconductivity of single crystals of the ceramic superconductor.

The $EuBa_2Cu_3O_{7-x}$ ceramic was treated with hydrogen at pressures of 1.3–10.0 kPa and temperatures of 393–483 K.[116, 117] This did not change the superconducting transition temperature. However, the formation of hydride and hydroxide phases [*e.g.*, CuH_2, $Ba(OH)_2$ and others] on the granule surfaces resulted in a decrease in the fraction of the superconducting phase, modification of the Josephson contacts, an increase in their electric conductivity and a decrease in the percolation conductivity.

It was found for the first time that the dependence of the critical current I_c on the quantity of hydrogen absorbed by the $YBa_2Cu_3O_{7-x}$ ceramic is non-monotonic and passes through a maximum at low concentrations of the latter.[118] The position of the maximum depends on the specimen density and correlates with the minimum position on the electric resistance curve. Based on these data, the conclusion was made that the enhanced conductivity of the inter-granular layers at low concentrations of absorbed hydrogen is due to the reduction of oxides with hydrogen, which favours the formation of metallic copper and compaction of the layers between the granules, and due to additional ionic conductivity resulting from the presence of the H^+ and OH^- ions.

The superconductivity parameters of the $YBa_2Cu_3O_{7-x}$ ceramic depend strongly on the oxygen concentration in the material lattice. It is well known that the oxygen-deficient $YBa_2Cu_3O_6$ ceramic is a semiconductor and displays antiferromagnetic properties, while the superoxidised $YBa_2Cu_3O_7$ ceramic has metallic properties. The effect of hydrogen inclusion into the $YBa_2Cu_3O_{7-x}$ ceramic with various oxygen contents at a temperature of 441 K in the pressure range from 1 to 3 atm was studied by the muon spin rotation method.[119] It was shown that hydrogen intercalation results in magnetic ordering of the copper atoms; the amount of hydrogen required for this depends on the oxygen index: the more oxygen the ceramic contains the more hydrogen is required. Thus, hydrogen intercalation results in a formal decrease in the oxygen index. This requires one hydrogen atom per two oxygen atoms. It was concluded that hydrogen in $YBa_2Cu_3O_{7-x}$ plays the role of an electron donor which decreases the number of holes.

The intercalation of hydrogen into the $YBa_2Cu_3O_{7-x}$ and $Bi_2Ca_2SrCu_2O_{8+x}$ ceramics at 473–503 K and at a pressure of 0.9 atm was studied.[120] The concentration of holes in the superconductors decreased in a ratio of one hole per one hydrogen atom upon hydrogen intercalation. In addition, the superconducting transition temperature depended strongly on the position occupied by hydrogen in the lattice. It was thus concluded that T_c is primarily determined by the mobility of holes in the CuO_2 planes. This was confirmed by an X-ray diffraction study of the $EuBa_2Cu_3O_{7-x}$ ceramic.[121] It was shown that the penetration of hydrogen into the material crystal structure along the CuO_2 planes begins at relatively low temperatures, 393–423 K, and at pressures of 5–10 kPa. A strong decrease in the thermal expansion factor was observed, which is believed to result from changes in the electronic structure of the material and the metal–dielectric

transition due to a decrease in the concentration of the oxygen vacancies.

A more detailed analysis of the hydrogen effect on the structure of yttrium and bismuth ceramics was made.[122] The inclusion of hydrogen results in structural changes in the $YBa_2Cu_3O_{7-x}$ lattice depending on the oxygen index.[123–125] Subsequent saturation of the ceramic with hydrogen results in the formation of amorphous hydride phases where hydrogen occupies interstitial positions. A solid solution of hydrogen in the ceramic, similar to metal–hydrogen solid solutions, can be formed.

According to NMR data,[126] the diffusion of hydrogen into the $YBa_2Cu_3O_{7-x}$ ceramic occurs on the oxygen vacancies in the Cu–O chains and along the *a* or *b* axes on the interstices in the Y planes. The activation energies of these processes are 0.29 and 0.25 eV, respectively. The diffusion of hydrogen ceases following exposure of the ceramic to hydrogen at room temperature for three to four months, and the hydrogen atoms form strong O–H bonds. It was found by ^1H NMR spectroscopy that hydrogen diffusion also occurs in hydrogenated $YBa_2Cu_3O_{7-x}$ ceramic at $T < 200$ K.[127] At temperatures from 130 to 92 K, the hydrogen atoms are mostly localised at the O(4) and O(5) lattice points. The inelastic neutron scattering and diffraction methods afforded the vibration spectra of hydrogen atoms in $YBa_2Cu_3O_{7-x}$ ceramic treated with hydrogen at 373 K.[128] Only several percent of the absorbed hydrogen participated in the formation of a solid solution; the H atoms occupy the octahedral positions formed by four Y atoms and two Cu atoms at the Cu(2) positions (Fig. 4). The rest of the hydrogen atoms are involved in an amorphous non-superconducting phase.

The NMR and X-ray diffraction methods were used to study the absorption of hydrogen and deuterium with the $YBa_2Cu_3O_7$ and $YBa_2Cu_3O_6$ ceramics at 473 K.[129] The incorporation of the hydrogen isotopes into $YBa_2Cu_3O_7$ results in partial removal of the chain oxygen from the O(1) positions and formation of O–H bonds. No new bonds are formed in the $YBa_2Cu_3O_6$ ceramic, and no changes in the lattice parameters with increase in the hydrogen content are observed.

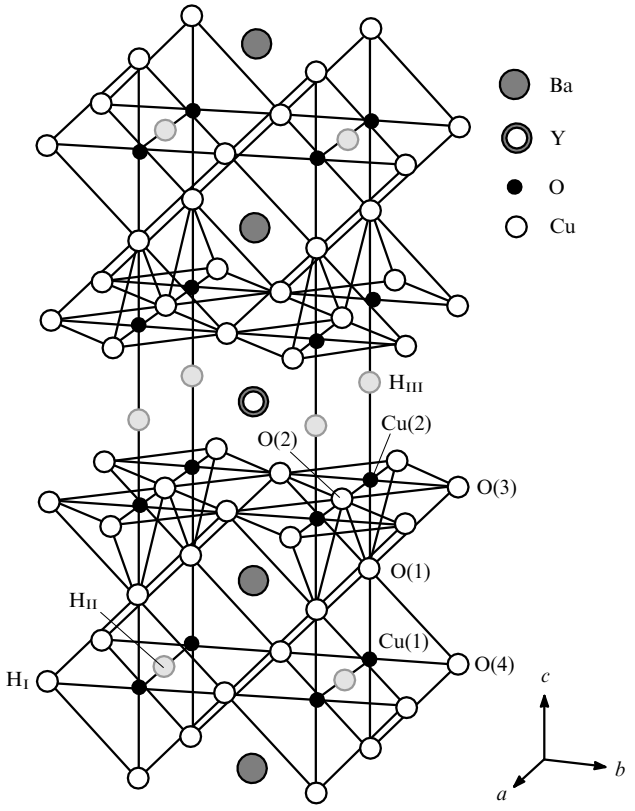


Figure 4. Possible locations of hydrogen atoms in the crystal lattice of $YBa_2Cu_3O_{7-x}$.[138]

Pre-treatment of an yttrium HTSC ceramic *in vacuo* followed by treatment with hydrogen at 400–600 K and 2.6 kPa caused a considerable decrease (by 150 K) in the temperature at which oxygen enters the tetragonal $YBa_2Cu_3O_{7-x}$ phase.[130] The specimen became a superconductor ($T_c = 80$ K) after such low-temperature intercalation of oxygen; the 'width' of transition into the superconducting state was 15 K. If treatment of the specimen with oxygen is carried out at the same temperatures immediately after evacuation, it does not become a superconductor. It was shown [131] that the decrease in the temperature at which oxygen enters the ceramics is caused by the transformation of the tetragonal phase of $YBa_2Cu_3O_{7-x}$ into the orthorhombic phase upon hydrogen treatment. The lattice parameter *b* decreases in this case since the hydrogen atoms occupy the oxygen vacancies along the direction *b* in the plane formed by CuO chains. Nevertheless, superconductivity is absent down to 4.2 K on cooling of the ceramics treated only with hydrogen. This is explained [131] by the small orthorhombic parameter *R* which is 10^{-3} for the hydrogenated ceramics, whereas it is above 3×10^{-3} for the superconducting yttrium ceramics.

Similar changes in the physicochemical properties were observed upon treatment of superconducting bismuth oxides. The fraction of the superconducting phase and the superconducting transition temperature were found to decrease upon reduction of a $Bi_2Sr_2CaCu_2O_z$ single crystal with hydrogen (a 10 : 90 $H_2 : N_2$ mixture) at 673 K.[132] Analysis of the X-ray absorption spectra led to the conclusion that reduction with hydrogen decreases the formal oxidation state of copper and the number of holes in the CuO_2 planes; this is the reason for the decrease in T_c.

In a study of the effect of hydrogen treatment on the structure of the bismuth-containing HTSC ceramic, the specimens were kept for several hours in a stream of hydrogen at 573 K.[133] Measurements of the electric conductivity of the specimens showed that the ceramic loses superconductivity completely and becomes a semiconductor. Hydrogenation of the ceramic results in a decrease in the unit cell volume, as shown by X-ray diffraction analysis. It should be noted that, on the contrary, hydrogenation of the yttrium HTSC ceramic increases the unit cell volume.

Thus, the type of effect of hydrogen on the properties of an HTSC material depends strongly on the treatment mode and temperature. At relatively low temperatures (up to 473 K), hydrogen mostly reacts with the granule surfaces and forms amorphous hydride phases involving metal atoms of the ceramic. In some cases, insignificant intercalation of hydrogen into the crystal structure of the material is observed. This phenomenon is accompanied by degradation of the magnetic properties of the superconductor and a decrease in the transport current density. As a rule, the superconducting transition temperature changes only slightly.

As the temperature of hydrogen treatment is increased, the superconductivity of HTSC materials decreases abruptly, until it is lost completely. This results from the incorporation of hydrogen into the crystal structure of the material which changes the T_c and the formal oxidation state of copper and decreases the concentration of holes in the CuO_2 planes.

High reactivity of hydrogen in the 400–470 K range found in a series of studies [134–136] gives reasons to assume that the protonic conductivity of hydrogen-containing barium–yttrium cuprates is rather high. However, the originally high metallic conductivity of cuprates of the $LnBa_2Cu_3O_7$ family (where Ln indicates yttrium or another rare-earth element) 'masks' strongly weaker ionic conductivity. Studies of hydrogenated cuprates of the general formula $H_yYBa_2Cu_3O_{7-x}$ showed [137] that their specific resistivities increase by almost six orders if the hydrogen index *y* increases from 0 to 2 and decrease by three orders upon oxidation of the ceramics with $y = 2$ if the *x* index changes from 0.1 to 0.8.

Almost all aspects of the physicochemical interaction of hydrogen with superconducting cuprates were covered in one of the latest reviews on the effect of hydrogen on HTSC materials.[138] Figure 4 shows the crystal structure of the orthorhombic phase of $YBa_2Cu_3O_{7-x}$ with indication of the positions where the hydrogen atoms are localised according to numerous studies. One can see that the intercalation of hydrogen atoms occurs along three main directions, *i.e.*, into the copper–oxygen bridges, chains and oxygen vacancies. However, the conductive CuO_2 layers remain unaffected. Hence, the observed changes in the electrophysical properties of HTSC materials are due to the electron density redistribution between the CuO_2 layers and the copper–oxygen chains O–Cu(1)–O–Cu(1)–O. As a rule, hydrogen intercalation into HTSC materials suppresses the superconductivity, while the superconducting transition temperature decreases (with rare exceptions). Figure 5 shows the dependence of the temperature of the onset of superconducting transition $T_{c,on}$ of an $H_yYBa_2Cu_3O_{7-x}$ thin film on the hydrogen content. If the hydrogen concentration increases, $T_{c,on}$ decreases monotonically, while the transition width increases from 0.8 to 6.2 K. It should be noted that at the hydrogen content of ~ 0.3 atoms per cell, a sharp bend of the curve is observed; this correlates with the bend on the dependence of T_c on the oxygen content (see Fig. 2). This probably indicates that the hydrogen atoms (donors) react readily with weakly bound oxygen ions (electron acceptors), thus changing the concentration of the current carriers in the HTSC material.

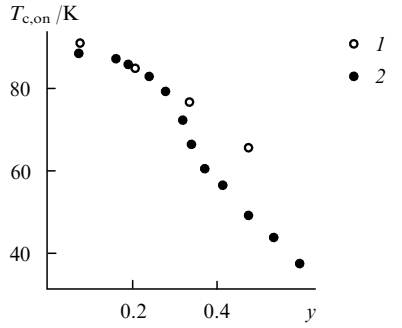


Figure 5. Dependence of the temperature of the onset of superconducting transition ($T_{c,on}$) of thin $H_yYBa_2Cu_3O_{7-x}$ film on the hydrogen content (y) in unit cell;[138] (*1*) from electric resistance measurements; (*2*) from magnetic susceptibility measurements.

3. The effect of halogens

Numerous studies on the effect of the crystal structure and oxidation states of the chemical elements constituting an HTSC material on superconductivity showed that the holes serve as charge carriers in the superconducting state; these holes are genetically related to the *p* states of the oxygen ions, and their concentration is an important characteristic of a superconductor.[139, 140] It thus follows that the anionic sublattice plays an essential role in superconductivity. One of the ways for changing the anionic sublattice defectivity involves doping with other anions, *e.g.*, halides.

The disappearance of electrical resistance at 155 K on $YBa_2Cu_3O_{7-x}$ specimens synthesised with the use of BaF_2 as one of the starting reagents was detected for the first time in 1987 (Ref. 141). Since that publication, numerous studies on the replacement of the anionic sublattice by halogens have appeared. The presence of fluorine can both improve superconductivity[142–149] and impair it.[150, 151] For example, treatment of the $YBa_2Cu_3O_{6.7}$ ceramic with $T_c = 65$ K with NF_3 at 613 K and with CCl_4 at 523–573 K increased T_c to 90 K in both cases.[152] Presumably, the halogen atoms are incorporated in the O(4) position along the CuO chains, *i.e.*, in a sense, halogenation is similar to saturation of oxygen-deficient ceramics with oxygen. If treatment is continued, the halogen anions occupy the O(5) positions but T_c is not increased any more. The effect of 'soft' fluorination on the degradation of powders of the $YBa_2Cu_3O_{7-x}$ composition in a humid atmosphere was studied.[153] The fluorination of powders was carried out in 49% hydrofluoric acid vapour at room temperature in a closed vessel. The physical properties and superconductivity of the powders were almost unchanged, but their stability in humid atmosphere increased considerably. This phenomenon is rationalised as being due to the higher stability of the resulting fluorides, BaF_2 and CuF_2, to water and prevention of further interaction of water with the superconductor granules. The presence of barium fluoride in synthesised thallium-containing ceramic cuprates with composition $TlBa_2Ca_2Cu_3O_x$ doped with zirconium, hafnium, ruthenium and tin oxides improved their critical parameters noticeably.[154] However, there is no satisfactory explanation of the effect of barium fluoride on the properties of thallium-containing cuprates.

In a continuation of this work, the composition and properties of thallium-containing HTSC ceramics obtained in the presence of metal fluorides were studied.[155] The specimens modified in this way are characterised by higher content of the superconducting phase, smaller granule sizes and more pronounced transition in the superconducting state in comparison with the specimens obtained under the same conditions but without addition of fluorides.

Enrichment of the $(Tl_{0.5}Pb_{0.5})Sr_{1.6}Ba_{0.4}Ca_2Cu_3O_z$ ceramic with fluorine carried out by the addition of CuF_2 during the synthesis improves considerably its superconductivity.[156] The superconducting transition temperatures increase from 120 to 125 K, and the critical current density increases by 300%. According to X-ray diffraction data, the fluorine atoms replace the oxygen atoms in the CuO_2 plane. Changes in the morphology of the specimens due to the increase in the ceramic granule sizes are observed. The increase in T_c is explained [156] by optimisation of the concentration of charge carriers in the CuO_2 plane by the fluorine atoms, whereas in ceramics devoid of fluorine, the concentration of these carriers is apparently far from optimum because of the high oxygen content.

NMR and EPR spectroscopic methods were used to study the intercalation of halogens into the crystal lattice of $YBa_2Cu_3O_{7-x}$.[157] The halogenation was carried out by exposing the specimens in a stream of gaseous NF_3 or CCl_4 diluted with N_2 at 573 and 523 K, respectively. The intercalated chlorine atoms are inserted in the chains between two copper atoms, while the fluorine atoms occupy the oxygen vacancies, as follows from the higher fluorine concentration in the materials with smaller oxygen indices.

The mechanism of the formation of halogen-containing HTSC phases based on $YBa_2Cu_3O_{7-x}$ was studied.[158] The intercalation of halogens (Cl_2, Br_2, I_2) into the $YBa_2Cu_3O_{7-x}$ lattice was carried out in the temperature range of 423–523 K. An X-ray anomalous dispersion and Mössbauer spectroscopic studies of the specimens obtained showed that the interaction of halogens with the tetragonal phase of $YBa_2Cu_3O_{7-x}$ occurs as intercalation of halogens into the anionic vacant positions of the Cu(1) layer (see Fig. 1 *b*). Charge transfer from the CuO_2 plane to halogens results in the formation of holes, which favours the manifestation of superconductivity ($60 < T_c < 93$ K) acquired by the resulting intercalation compounds. The chloride anion, unlike other halide anions, changes the ceramic's microstructure owing to its large size; this results in the formation of stresses and dislocations and manifests itself as a decrease in the critical current. A study of the surface layers of the $YBa_2Cu_3O_{7-x}$ tetragonal phase after its bombardment with chloride ions showed that implantation of chloride anions results in the formation of a orthorhombic phase layer near the surface; its thickness approximately equals the anion penetration depth.[159] This layer has the properties of a superconductor with a critical temperature of *ca.* 70 K.

In a study of chlorine-containing phases of the type $YBa_2Cu_3O_{7-x}Cl_y$ synthesised with the use of PCl_5 as a chlorinat-

ing agent, it was assumed [160] that at low temperatures the halogens are localised in chains around the copper atoms Cu(1) and the O(5) vacant positions are occupied first. An increase in the halogenation depth results in replacement of the O(4) chain oxygen atoms. Further halogenation under more drastic conditions results in replacement of the O(1) atoms, and the resulting phase has the limiting composition $YBa_2Cu_3O_4Cl_4$. The conclusion was made [160] that the decisive role in maintaining the superconductivity of halogen-containing phases belongs to the nature of the bridging atoms located at the O(1) position, which link the CuO_2 layers to the Cu(1) chain atoms: the electron-withdrawing properties of these bridging atoms induce superconductivity.

The change in the superconducting transition temperature due to the intercalation of $HgBr_2$ into polycrystalline $Bi_2Sr_{1.5-y}La_yCa_{1.5}Cu_2O_x$ specimens with $0.0 \leqslant y \leqslant 0.4$ was studied.[161] The specimens were obtained by keeping a tube containing certain weighed samples of $HgBr_2$ and the original superconducting ceramic at 508 K for 4 h *in vacuo*. An X-ray diffraction study showed that $HgBr_2$ is intercalated between the Bi–O planes. Figure 6 shows the dependence of T_c on y for the original and treated specimens. One can see that after treatment T_c decreases for the specimens with $y < 0.2$ and increases for the specimens with $y > 0.2$. It is believed that the intercalation of $HgBr_2$ changes the charge on the copper ions located in the conducting planes. The correlation relationships between the change in the copper charge (Δn) and T_c are reported;[161] it follows from this relationship that Δn depends linearly on the concentration of the added compound and correlates with the concentration of the charge-carrying holes.

Upon treatment of non-superconducting ceramic specimens of $YBa_2Cu_3O_{7-x}$ (tetragonal phase) with bromine vapour at 503 K and iodine vapour at 673 K without contact with air, they acquired superconductivity; the T_c values were 80–85 and 55 K, respectively.[162]

The chemical interaction of iodine with the lattice copper ions can be a possible reason for the appearance of superconductivity in iodinated specimens. A similar assumption was made in a Raman spectroscopic study of the tetragonal $YBa_2Cu_3O_{6.1}$ ceramic treated in a iodine atmosphere. Iodine reacts with copper to 'extract' it from the lattice.[163] Oxygen is redistributed over the lattice, occupies the vacant sites in the chain and thus provides the possibility for superconductivity to occur. The same conclusion was also made in yet another study.[164] X-Ray diffraction analysis performed after annealing of the non-superconducting phase $YBa_2Cu_3O_6$ in iodine vapour at 553–653 K showed that the superconducting orthorhombic phase had appeared and reflexes of foreign phases were detected, which possibly corresponded to copper, barium and yttrium iodides. Treatment of the $YBa_2Cu_3O_7$ orthorhombic phase under similar conditions was not accompanied by either structural parameter changes or formation of foreign phases. Annealing a powder mixture of the $YBa_2Cu_3O_6$ and $YBa_2Cu_3O_7$ phases *in vacuo* at 493 K (which is much lower than the temperature of oxygen liberation, 623 K) was accompanied by the intergranular oxygen transfer from the $YBa_2Cu_3O_7$ phase to the $YBa_2Cu_3O_6$ phase and resulted in a phase with composition $YBa_2Cu_3O_{6.65}$. This suggests the high diffusion mobility of oxygen at low temperature in the lattices of the ceramics studied.

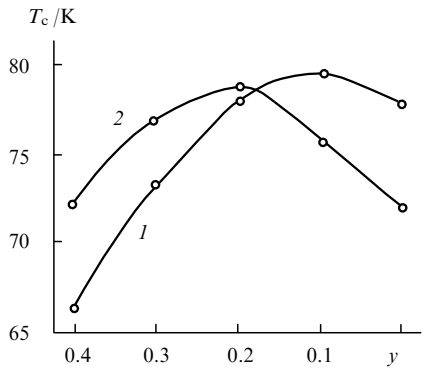


Figure 6. Dependence of the superconducting transition temperature of the $Bi_2Sr_{1.5-y}La_yCa_{1.5}Cu_2O_x$ ceramic on y;[161] (*1*) starting specimen; (*2*) sample after treatment with $HgBr_2$.

Thus, the basic mechanism of the effect of iodine on the superconducting properties of yttrium ceramics apparently involves oxygen transfer into the tetragonal phase; this oxygen can be liberated from the neighbouring phases under the effect of halogen atoms. Treatment of the tetragonal phase with iodine vapour at 543 K resulted in a continuous series of $YBa_2Cu_{3-y}O_xI_z$ solid solutions which possessed superconductivity.[165] The reaction of iodine with the crystal lattice of $YBa_2Cu_3O_{7-x}$ single crystals depends essentially on the initial oxygen content.[166] At the maximum oxygen content (the specimen with $T_c = 92$ K), no reaction of the crystals with iodine was observed. However, the stoichiometric cationic compositions of the crystals of orthorhombic ($T_c = 55–60$ K) and tetragonal phases changed and an amorphous layer of varying thickness was formed on the surface; this was followed by complete destruction of the specimens. The penetration of iodine into the matrix was determined by the presence of oxygen vacancies in the principal planes. Ordering of the iodine atoms included in the crystal lattice was not observed.

Two-phase specimens were formed upon bromination: the original tetragonal phase coexisted with a orthorhombic phase in the ratio $\sim 1:1$. The iodinated specimens consisted completely of a orthorhombic phase. The parameters of the orthorhombic phases in the iodinated and brominated specimens are similar. Thus, the halogen atoms occupy presumably the vacancies of the O(4) type along the b axis (see Fig. 1 *b*).[162] It was assumed on the basis of EPR spectra that halogenation results in the transfer of negative charge to the CuO chains and formation of holes at the CuO_2 planes.

A study of iodine intercalation at 23 K into the $Bi_2Sr_2Ca_{1-y}Y_yCu_2O_8$ ceramic by X-ray diffraction analysis showed that iodine is incorporated in the BiO–OBi double layers in such a way that the distance between them increases.[167] The superconducting transition temperature decreases by 10 K because the concentration of the hole carriers exceeds the optimum level.

The effect of iodine and oxygen intercalation on the physical properties and superconductivity of $Bi_2Sr_2CaCu_2O_{8+x}$ single crystals was studied.[168] The starting single crystals and elementary iodine were sealed in an evacuated glass tube, heated to 453 K and kept for 330 h at the same temperature. The oxidation of single crystals with oxygen was carried out at 10 atm and 823 K for 140 h, or at 600 atm and 673 K for 320 h. The resistance and magnetic measurements of the thus treated samples showed that the dimensionality of the superconducting system changes from two to three, T_c decreases, and the activation energy of magnetic flux creep changes. According to the model suggested for the explanation of these phenomena, the HTSC material acquires a multilayered structure with alternation of the superconducting and normal layers due to the intercalation of iodine and oxygen. The 'proximity' effect results in the redistribution of the charge carriers between the layers and hence in changes in the physical properties and superconductivity parameters. The structural ordering of atoms in superconducting $Bi_2Sr_2CaCu_2I_yO_x$ single crystals containing intercalated iodine was studied by low-energy electron diffraction, Auger and photoelectron spectroscopy on chipped surfaces, as well as by transmission electron spectroscopy.[169] It was shown that iodination results in a superstructure with ordered aggregates of iodine molecular complexes in the empty channels formed upon distortion of the original lattice by structural modulation.

In yet another study,[170] the intercalation of iodine in bismuth-based ceramics was carried out in a sealed tube, which was heated to 458 K over a period of 6 h and kept for 240 h at this temperature. According to the nuclear quadrupole resonance data, the iodinated $Bi_2Sr_2CaCu_2O_x$ specimens contain no chemical bonds of the Bi—I and Cu—I types, *i.e.*, iodine in them is in atomic or molecular form and is truly intercalated. The superconducting transition temperature of the iodinated ceramic was 73 K.

Thus, halogenation of the yttrium-containing oxygen-deficient ceramic consisting of a $YBa_2Cu_3O_{6+x}$ tetragonal phase results in orthorhombic phases with $YBa_2Cu_3O_{6+x}Hal_y$ composition. The new phases have superconducting properties with approximately the same T_c as the usual superconducting ceramics, $YBa_2Cu_3O_{7-x}$. The iodinated ceramic is an exception, its T_c is no higher than the liquid nitrogen temperature. The formation of superconducting phases upon ceramics' halogenation is explained by inclusion of halogens at the oxygen O(1) positions; the halogens 'withdraw' the electronic charge from the CuO_2 planes onto themselves, which in turn increases the concentration of holes.

4. Degradation of high-temperature superconducting materials exposed to CO_2 and H_2O

Exposure of HTSC materials to atmospheric carbon dioxide and water results in their degradation accompanied by the loss of superconductivity and degradation of the superconducting phases. Therefore, the problem of storage and stabilisation of HTSC materials is of major importance. One of the first reviews on the chemical degradation of superconductors is found in Ref. 171.

The reaction of CO_2 with the $YBa_2Cu_3O_{7-x}$ ceramic starts at room temperature.[172] The decrease in the critical intergranular current correlates with the intensity of the CO_2^+ peak in the mass spectra of the gases evolved from the ceramic; this suggests that carbonates are localised at the granule boundaries. When synthesis is carried out in the air at high temperatures, $YBa_2Cu_3O_{7-x}$ absorbs CO_2. The maximum absorption is observed at 1173 K, and the amount of absorbed CO_2 with respect to carbon reaches 0.05% of the ceramic mass.[173] A study of the decomposition of the $YBa_2Cu_3O_{7-x}$ ceramic in a 5% CO_2 + 95% O_2 mixture at 1088 K showed that the nuclei of the $Y_2Cu_2O_5$ and $BaCO_3$ phases are initially formed very fast, and then a 'green' phase of Y_2BaCuO_5 and CuO appears. The formation of $BaCO_3$ at the boundaries between the granules upon treatment of $YBa_2Cu_3O_{7-x}$ with pure CO_2 at 1123 K for 2 h was reported.[174]

The powdered $YBa_2Cu_3O_{7-x}$ ceramic reacts with CO_2 at 1273 K both in the absence and in the presence of moisture to give decomposition products such as $BaCO_3$, $Y_2Cu_2O_5$, CuO, Cu_2O and Y_2O_3.[175] In the 90% CO_2 + 10% O_2 mixture, the decomposition products differ somewhat: they do not contain Cu_2O and Y_2O_3.

A detailed study of the kinetics of the reaction between powdered $YBa_2Cu_3O_{7-x}$ and pure CO_2 in the temperature range of 823–1163 K was carried out.[176] The reaction of the ceramic with CO_2 can be described by the equation:

$$2\,YBa_2Cu_3O_{7-x} + 3\,CO_2 = Y_2BaCuO_5 + 3\,BaCO_3 + 3\,CuO + Cu_2O + (1-x)\,O_2\,,$$

where Y_2BaCuO_5 is an intermediate. In the temperature range of 823–1088 K this reaction limits the overall rate of the process and has an order of 1.5 with respect to the ceramic; its activation energy is 95 kJ mol^{-1}. Subsequent 'carbonisation' of the ceramic occurs according to the equation:

$$Y_2BaCuO_5 + CuO + CO_2 = Y_2Cu_2O_5 + BaCO_3\,.$$

The presence of an alkaline-earth element in the HTSC ceramics provides a material with basic properties and hence makes it capable of absorbing CO_2 when in contact with air.

Calcination of the $YBa_2Cu_3O_{7-x}$ ceramic during synthesis at 1223 K in air containing more than 1% carbon dioxide results in a non-superconducting tetragonal phase.[177] It is formed due to hindered oxygen exchange because of the formation of carbonate films on the material surface. The carbonates and decomposition products are mainly formed at the granule boundaries; this decreases considerably the critical intergranular current of the superconductor.

In the initial stage of the reaction of $YBa_2Cu_3O_{7-x}$ with water vapour and carbon dioxide, the kinetics of water sorption is consistent with a process occurring at the internal grain boundaries and it is well described by a first order equation.[178] The diffusion of water vapour to the internal layers of the ceramic is the rate-determining step for CO_2 transfer. If the ceramic is pretreated with water vapour, the CO_2 transfer occurs extremely quickly and is characterised by an effective diffusion factor exceeding 10^{-6} cm^2 s^{-1}. This is assumed to be due to water vapour condensation in the material pores.

Prolonged annealing of a $Bi_{1.6}Pb_{0.4}Sr_{1.7}Ca_{2.3}Cu_{3.0}O_{10+x}$ powder at 1123 K decreased slightly the carbon content in the specimen from 0.02 mass % after 24 h to 0.01 mass % after 192 h.[179] The powdered HTSC ceramic quickly absorbs carbon dioxide if stored in air: the content of carbon in the ceramic increases by a factor of two in 15 h, reaches 0.1 mass % in 240 h and then remains almost unchanged. An increase in the carbon content in bulk specimens from 0.019 mass % to 0.13 mass % is accompanied by a decrease in the critical current density from 280 to 150 A cm^{-2}.

The $YBa_2Cu_3O_{7-x}$ ceramic readily reacts with water vapour even at room temperature to form the 'green' phase Y_2BaCuO_5 according to the equation:[180, 181]

$$2\,YBa_2Cu_3O_{7-x} + 3\,H_2 = 5\,CuO + 3\,Ba(OH)_2 + Y_2BaCuO_5 + (0.5-x)\,O_2\,.$$

If this occurs in the presence of CO_2, the resulting barium hydroxide immediately reacts with carbon dioxide:[182]

$$CO_2 + Ba(OH)_2 = BaCO_3 + H_2O\,.$$

Thus, in this case water acts as a catalyst of carbonate formation.

Owing to the high basicity of barium oxide, $YBa_2Cu_3O_{7-x}$ can react with CO_2 in humid atmospheres even at very small CO_2 partial pressures.[183] The products of hydration ageing of the $YBa_2Cu_3O_{7-x}$ ceramic were studied.[184] The morphology of the new formations was studied using a scanning electron microscope. The original grain surface was rather smooth, but small protrusions and cracks appeared there after exposure to water vapour for one hour. If exposure was increased to 2.5 h, the ceramic's grains became covered with thin needles. An even longer exposure promoted the integration of the new formations which gradually covered the entire grain surfaces. X-Ray diffraction analysis showed that the new formations consist of barium hydroxide, α-$Ba(OH)_2$, and the Y_2BaCuO_5 'green' phase.

Similar studies carried out using electromagnetic radiation absorption in the range of 1–3 MHz made it possible to follow the character of intergranular medium changes in specimens of the $YBa_2Cu_3O_{7-x}$ ceramic exposed to moisture.[185] The changes in the chemical composition (degradation) of certain granules can occur at a depth of 0.3–1.0 μm from the surface depending on the specimen density. The formation of such a layer interferes with subsequent changes. Noticeable degradation of specimens with a density above 5.4 g cm^{-3} is observed in water after 10 h whereas in ordinary atmosphere it takes 5 months. Subsequent exposure to water little affects the superconductivity characteristics of the specimens.

The surface state and microstructure affect the reaction of the $YBa_2Cu_3O_{7-x}$ ceramic with water.[186] Generally, the average pore size in the $YBa_2Cu_3O_{7-x}$ ceramic is $\sim$ 1 μm at an average grain size of 3–20 μm.[187] Analysis of data on small angle neutron scattering at the liquid nitrogen temperature led to the conclusion

that the majority of pores in the yttrium ceramic are open.[188] Thus, water can react not only with the outer but also with the inner surface by penetrating through the open pores. Water diffusion is an activation process. The activation energy is ~ 0.033 eV, this order of magnitude corresponding to the energy of a thermal quantum. Surface polishing of pellets of a sample accelerates the degradation three- to five-fold; apparently, this is caused by an increase in the number of open pores connected to the surface as a result of polishing. Hydration of textured specimens is strongly hindered, probably due to the small number of boundaries because of strong binding between the oriented grains, the concentration of oxygen vacancies in the intergranular spaces is rather small, and penetration of hydroxy groups inside the pellet is hindered. The penetration depth of water molecules into a textured specimen after ageing in water for 10 h at room temperature is 5 times smaller than the depth of its penetration into an isotropic ceramic.

Isothermal oxidation of hydrated $YBa_2Cu_3O_{7-x}$ ceramic is accompanied by a stepwise increase in the sample mass, which indicates the presence of two oxidation steps, 'slow' and 'fast'.[189] The oxidation rate decreases proportionally to the water concentration in the material. The OH^- ions play a role of stoppers for defects of different dimensionality (oxygen ions, twinning structure boundaries) in their movement through the $YBa_2Cu_3O_{7-x}$ lattice. Presumably, during the 'slow' oxidation stage of the yttrium ceramic, the boundaries of the twinning structure between the crystallites of this compound are in the state of accelerated movement due to thermal activation and 'stripping' of these boundaries from localised proton-containing ions in the near-surface zone. Subsequent movement of these boundaries occurs in the matrix free of impurities.

The $YBa_2Cu_4O_8$ ceramic and $YBa_2Cu_3O_{7-x}$ specimens with an admixture of silver are much more stable against moisture than non-doped $YBa_2Cu_3O_{7-x}$ ceramic.[190, 191] This is explained by a more compact arrangement of granules consolidated by metallic silver particles in doped ceramics; this evidently interferes with fast diffusion of the water molecules in the material bulk. The effect of silver on the stability of powders with composition $YBa_2Cu_3O_{7-x}$ in a humid atmosphere was studied.[192] The composition of the surface was studied using an electron probe X-ray microanalyser and X-ray photoelectron spectroscopy. If the water content in the powder is above 1.6 mass %, silver (5 mass % – 15 mass %) has a stabilising effect. In order to increase the critical current, it is recommended to add 15 mass % of silver to the moist powder (1.6 mass % H_2O). On the surfaces of ceramics containing this amount of silver, the latter is present in the form of separate inclusions. At the Ag content of 5 mass % – 15 mass %, superconductivities of the ceramics remain practically the same as those for the original $YBa_2Cu_3O_{7-x}$ specimen.

If the $EuBa_2Cu_3O_{7-x}$ ceramic is treated with water, the evolution of oxygen is preceded by dissolution of an insignificant amount of Ba^{2+} ions ($\sim 7\%$ of the total amount of barium in the ceramic).[193] The europium ceramic is much more stable than the $YBa_2Cu_3O_{7-x}$ ceramic, which undergoes 50% decomposition in a humid atmosphere at room temperature. Noticeable decomposition of $EuBa_2Cu_3O_{7-x}$ (*i.e.* evolution of gaseous O_2 and passage of Ba^{2+} cations into solution) starts 2 h after the contact with water at 333 K and occurs according to the equation:

$$2EuBa_2Cu_3O_{7-x} + 3H_2 = 5\,CuO + 3\,Ba(OH)_2 + Eu_2BaCuO_5 + \\ + (0.5-x)\,O_2\,.$$

The decomposition of the ceramic at 353 K starts almost immediately. Complete reduction of Cu^{3+} to Cu^{2+} occurs only at 373 K. The decomposition of the $YBa_2Cu_3O_{7-x}$ ceramic in distilled water and in solutions of sodium sulfate and barium chloride was studied.[194] It was shown that the presence of barium ions interferes with the hydrolytic decomposition of $YBa_2Cu_3O_{7-x}$; after treatment with 10^{-2} M aqueous solution of $BaCl_2$, the ceramic retains superconductivity even after boiling. Hydrolysis of the ceramic is accompanied by leaching of barium cations, and addition of sulfate ions to water which binds barium ions causes complete decomposition of the superconductor. This is explained by equilibrium displacement upon changes in the reaction product concentration in accordance with the thermodynamic laws.

An interesting feature of the behaviour of water present in the $YBa_2Cu_3O_{7-x}$ ceramic was noted.[195] It was found that the superconducting phase cannot release water at temperatures of oxidative annealing (673 – 873 K). It is believed that this results from geometrical factors related to lattice distortion as a result of oxidative annealing, which hinders the exit of proton-containing ions from the O(5) positions.

It was found by thermal desorption methods that water on the surface of the $YBa_2Cu_3O_{7-x}$ ceramic can be physically adsorbed and structurally bound (in the latter case, the bond energy equals 145 kJ mol^{-1}).[196, 197] The water molecules can occupy two types of positions, *viz.*, the position in the yttrium plane between the CuO_2 planes and the position between two Cu(1) copper atoms (see Fig. 4).

EPR studies showed [198] that inclusion of water molecules into the $YBa_2Cu_3O_{7-x}$ lattice results in the appearance of the Cu^{2+} paramagnetic centres at the Cu(2) positions in the CuO_2 layers. The EPR signal intensity depends on the water content in the ceramic. It is assumed that these paramagnetic centres are formed due to non-uniform deformation along the CuO_2 plane rather than due to decomposition of the material.

A radiothermoluminescence study of the moisture-induced degradation of the $RBa_2Cu_3O_{7-x}$ type HTSC materials (R = Y, Sm, Eu, Ho) showed that barium hydroxide is the compound responsible for radiothermoluminescence.[199] The radiation intensity is much lower if the specimen contains a minor amount of the original compounds which did not react under the conditions of solid-phase synthesis of the HTSC material.

The possibility of protection of materials based on $YBa_2Cu_3O_{7-x}$ from degradation in water vapour by applying coatings of paraffin, poly(vinylbutyral) and oxidised triglycerides of unsaturated fatty acids was studied.[200] The last named was found to be the most effective.

5. The effect of Ar, He and N_2 adsorption

Noble gases, *viz.*, Ar and He, as well as N_2, do not react chemically with the material, and hence, the major factors of their effect on superconductivity can involve inclusion into the crystal structure of the material or surface 'charging' due to adsorption.

The effect of argon on the electric conductivity of the $YBa_2Cu_3O_{7-x}$ ceramic was studied.[110] The specimens were kept for several days *in vacuo* (10^{-3} Pa) at room temperature, then purged for three days with pure argon at the same temperature. After that, they were analysed by the resistance method at currents of 50, 500 and 5000 μA. An abnormal dependence of the electric conductivity on temperature was found when the latter was increased from 200 to 300 K: the resistance of a sample abruptly almost doubled at a current of 50 μA; the increase was only several percent at 500 μA, whereas no abnormal increase in resistance at all was observed at 5000 μA. Apparently, this dependence of the electric resistance on current in this temperature range cannot be due to any manifestation of superconductivity. An increase in the current flowing through a superconducting specimen should result in the violation of the superconducting state and in the increase in resistance, rather than in the opposite effect observed in the experiment.

An Auger scanning microscopic study of specimens treated with argon revealed the presence of argon atoms in the near-surface layer (~ 100 Å). The observed phenomenon is explained [110] by the oxygen disordering in the lattice on the superconductor surface and the formation of a tetragonal non-superconducting phase, which is responsible for the resistance increase, in the gaps between the granules. However, the resistance of the specimens treated with argon decreased with a decrease in

temperature. Apparently, this is due to the fact that below room temperature, oxygen and oxygen vacancies can become ordered, and the semi-conducting tetragonal phase can be transformed to the orthorhombic phase, which displays metallic properties.[201]

An increase in T_c and J_c due to intercalation of simple gases into HTSC ceramics was observed repeatedly.[110,202–204] However, no reliable information on this phenomenon is available so far. Apparently, this can be associated with a very strong dependence of superconductivity of a material on its structure; because of this, small and hardly controlled changes in the crystal lattice parameters due to intercalation can change essentially the properties affecting superconductivity.

A substantial increase in T_c was observed upon low-temperature ($\sim$ 78 K) treatment of the $YBa_2Cu_3O_{7-x}$ superconductor in N_2, Ar, O_2 and He streams.[203] In particular, T_c increased from 90 to 141 K upon treatment with nitrogen. Treatment with hydrogen did not affect T_c. The change in the superconducting transition temperature correlates with the duration of treatment. The change in the parameters of $YBa_2Cu_3O_{7-x}$ superconductivity was assumed to be due to the inclusion of the gas molecules in the superconductor lattice. This changes the energetic state of the lattice and hence increases the energy of interaction between the carriers of superconductivity current, *i.e.*, the Cooper pairs. If the temperature increases, the gas starts to desorb; the Cooper pairs become unstable, and the superconductor passes in the normal (non-superconducting) state. However, it is unclear from this explanation why gases as different in nature as nitrogen, argon, oxygen and helium behave similarly. It is known, for example, that helium is not adsorbed at all on solid surfaces at the liquid nitrogen temperature.[205]

In at attempt to reproduce the effects described above, Granados *et al.*[206] failed to observe an increase in T_c during low-temperature treatment of the $YBa_2Cu_3O_{7-x}$ ceramic with helium. Therefore, the results considered above are attributed to experimental errors. A reason for the T_c increase could involve the rather fast heating of the specimen, which at certain helium pressures usually results in overestimation of T_c in resistance measurements.

Low-temperature treatment (77.4 K) of the $YBa_2Cu_3O_{7-x}$ ceramic with nitrogen at normal pressure and with hydrogen at pressures up to 300 atm resulted in changes in T_c which increased or decreased depending on the duration of treatment.[204] Similar results were obtained upon treatment of $YBa_2Cu_3O_{7-x}$ with benzonitrile. After keeping the specimen in liquid benzonitrile for 11 h at room temperature, the T_c increased by 2 K. The T_c value was determined by measuring the electric resistance and magnetic susceptibility of a superconductor heated from 77.4 to 100 K. After several measurements, the original T_c value was almost restored. The similar effect of foreign molecules with completely different chemical properties on the superconductivity of the oxide $YBa_2Cu_3O_{7-x}$ led to the conclusion [204] that foreign molecules penetrate into the ceramics due to diffusion along the granule boundaries and microcracks, thus creating mechanical stress.[207–209] The adsorbed phase propagating along the surface of a granule or a microcrack 'bursts open' the granules at the contact site, and the resulting mechanical stress can be quite strong. In the zones adjacent to the crack mouths, the ceramic material appears to be under huge pressure, which is believed to result in a local change in the superconducting transition temperature.

IV. The effects of adsorption and intercalation of organic molecules on the properties of high-temperature superconductors

The effects of organic compounds on the properties of superconductors are considerably more diverse than those of simple molecules. They can affect HTSC materials due to a number of their specific properties (ability to form complexes with metal ions, to create regular layered structures that have electric conductivity, to be mechanically implanted in the superconductor material, to form charge transfer complexes), and also due to the possible presence of stable paramagnetic centres in their molecules.

1. Adsorption of organic compounds

The effects of adsorption of organic compounds on superconductivity was first studied on films of low-temperature metal superconductors.[210–214] The adsorption of 3,4,7,8-tetramethyl-1,10-phenanthroline (TMP) on a thin vanadium film increased the superconducting transition temperature by 0.09 K.[210] The assumption was made that this effect is caused by the electronic properties of the adsorbed molecule, namely, the electronegativity parameter

$$\psi = \frac{I + A}{2},$$

where I is the ionisation potential and A is the electron affinity.

Subsequent studies covered a much wider range of organic molecules of various nature with a very wide range interval of electronegativities (Table 1).[211–214] Thin vanadium and indium films ($\sim$ 10 nm thick) with T_c = 2.4 and 4.1 K, respectively, were used as superconductors. The films were obtained by vapour deposition of the pure (99.999%) metals in a high vacuum (10^{-6} Pa) onto a single-crystal quartz substrate. The molecules of organic compounds, mainly those with planar structures, were deposited on the films by evaporation *in vacuo* or by chemical methods. The superconducting transition temperatures and the critical currents before and after the adsorption were determined by the contact resistance method. For a vanadium film, good correlation was observed between the electronegativity and the sign of the T_c change upon adsorption of 14 different organic compounds. Adsorption of electron-donating molecules (anthracene, tetracene, perylene, *etc.*) with low electronegativity ($\psi \approx 3.9$ eV) caused an increase in T_c. Conversely, electron-acceptor molecules, for example, tetracyanoquinodimethane with $\psi \geqslant 5.5$ eV, decreased the T_c. Similar regularities were also noted for an indium film.

However, there are exceptions. For example, the superconducting transition temperature increased upon deposition of

Table 1. Changes in T_c upon adsorption of organic compounds on low-temperature metallic superconductor films and certain physicochemical parameters of these compounds.[214]

Adsorbed compound	T_c /K	ΔT_c /K	I /eV	A /eV	ψ /eV
Thin vanadium film					
Anthracene	2.33	+0.10	7.23	0.42	3.83
Tetracene	2.76	+0.075	6.88	1.0	3.94
Perylene	2.92	+0.08	7.15	0.85	4.0
Phenothiazine	2.20	+0.09	7.28	–	–
TMP	2.45	+0.09	8.65	–	–
2-Aminoanthraquinone	2.62	+0.06	< 9.34	< 0.5	< 4.9
1,4,5,8-Tetrachloro-anthraquinone	2.23	+0.025	> 9.34	0.66	> 5.0
Pyromellitic dianhydride	2.25	−0.11	–	0.85	–
TCQDM	2.25	−0.10	–	1.7	> 5.5
Tripyridyl-*s*-triazine	3.6	+0.05	–	–	–
Titanium dicyclopenta-dienyl dichloride	2.42	−0.05	–	–	–
Thin indium film					
TMP	4.1	0.00	8.65	–	–
TCQDM	4.09	−0.23	–	1.7	> 5.5

Note. TMP is 3,4,7,8-tetramethyl-1,10-phenanthroline; TCQDM is tetracyanoquinodimethane.

electron-accepting tripyridyl-*s*-triazine molecules on a vanadium film. The electron-donating TMP molecules affected vanadium and indium films differently: the adsorption of TMP on the vanadium film increased T_c, whereas that on the indium film did not change T_c.[214] This was explained by the formation of a 'metal atom – organic molecule' complex. In the case of vanadium, which is a transition metal, a bond is formed between an unoccupied *d* orbital and a molecular π orbital of the organic molecule; this favours the transfer of an electron to the superconductor film and hence changes its superconductivity. Unlike vanadium, indium does not have a similar *d* orbital, therefore TMP adsorption does not affect its properties.

In yet another work,[214] the effects of the adsorption of organic compounds on the critical current of superconducting films was also studied. The adsorption of electron donors, *viz*., tetracene and perylene, on a vanadium film resulted in an increase in the critical current. Although a rather good correlation exists between the electronegativity of organic molecules, ψ, and the critical parameters of superconductivity of the vanadium film, I_c and T_c, the detailed mechanism of this phenomenon remains unclear. This can be due to charging of the superconducting film surface upon adsorption of organic compounds. For example, is was shown [215] that the superconducting transition temperature of an indium film depends on the surface charge sign. A strong acceptor, TCQDM, 'withdraws' electrons from the superconductor bulk, the concentration of the charge carriers decreases, and T_c decreases by 0.23 K. A decrease in T_c was also observed in an external electrical field where the film surface was charged positively.

With the advent of oxide-based HTSC materials, research into the effect of adsorption of organic compounds on the critical parameters of superconductivity has gained new impetus. An organic dye, octaethylporphyrin, was applied onto a plate 3 mm long and 50 μm wide made of a 100 nm thick $YBa_2Cu_3O_{7-x}$ film on a MgO(100) single crystal substrate.[216] After cooling the specimen below T_c, the superconductor was irradiated, and the dependence of the current on the wavelength of incident light was measured. The system response to the light and the wavelength selectivity were much more significant at temperatures below T_c. The strongest response estimated as the current passing through the plate was observed at a wavelength of 600 nm corresponding to the maximum absorption of the dye.

The effect of a deposited conducting polymer, polypyrrole, on superconductivity of an $YBa_2Cu_3O_{7-x}$ film was studied.[217] The electric conductivity of the film at temperatures higher than T_c, as well as the T_c itself, depend on the electric properties of the polymer. The dielectric polymer little affects the electric properties of the film. The polymer in the conducting or oxidised forms decreases T_c of the superconducting film by 15 K. Chemical or electrochemical reduction of the polymer results in restoration of the original T_c value. In order to explain these phenomena, the authors put forward two assumptions: (1) the polymer in the oxidised state does not affect the concentration of weakly bound oxygen in the $YBa_2Cu_3O_{7-x}$ film, and hence the change in T_c is not related to oxygen; (2) the observed change in T_c is caused by the 'proximity' effect, *i.e*. partial penetration of the Cooper pairs into the conducting polymer layer.

In continuation of these experiments, temperature dependences of the contact resistance at the boundaries between the $YBa_2Cu_3O_{7-x}$, $GdBa_2Cu_3O_{7-x}$ and $Bi_{1.7}Pb_{0.3}Sr_{1.6}Ca_{2.4}Cu_3O_{10}$ HTSC ceramics, on the one hand, and the oxidised form of a deposited conducting polymer, poly(3-hexylthiophene), on the other hand, were studied.[218] The electric resistance of this contact decreases around T_c. It was assumed that ceramics in the superconducting state can induce a kind of superconductivity in the polymer, in other words, this phenomenon can be directly related to the 'proximity' effect.

Exposure of an $YBa_2Cu_3O_{7-x}$ powder to organic donor-acceptor electron-transport (DAET) systems (for example, DMF – CCl_4, 2,2′-bipyridyl – monoethanolamine, DMSO – CCl_4, *etc*.) was accompanied by partial etching of the ceramic without considerable change in its phase composition.[219, 220] Etching removes the labile near-surface oxygen and exposes the more perfect structured layers; the contact between the granules and their ability to sinter are improved. The concentration of oxygen in the material bulk does not change. Thus, etching of HTSC ceramics powder with DAET-systems under mild conditions results in modification of the surface layers of the species and is accompanied by stabilisation of the superconducting state and improvement of the superconductor quality.

Room-temperature treatment of an $YBa_2Cu_3O_{7-x}$ powder with an excess of 1-hydroxy-2,2,6,6-tetramethylpiperidine (HTMP), which is readily oxidised into a stable nitroxyl radical even on treatment with atmospheric oxygen, is accompanied by extraction of weakly bound oxygen from the specimen bulk.[221] An EPR study of the radical accumulation kinetics made it possible to determine the amount of the oxygen extracted and to estimate the activation energy of this process. The determined activation energy, ~ 16 kJ mol^{-1}, is comparable with E_a for the diffusion of highly reactive oxygen in $YBa_2Cu_3O_{7-x}$. It is much smaller than the values that characterise the evolution of weakly bound oxygen to the gas phase upon thermal desorption (at $x < 0.006$, $E_a = 120$ kJ mol^{-1}). Apparently, this difference can be explained by the fact that HTMP adsorbed on the ceramic lowers the activation barrier for oxygen exit from the surface layer of the specimen. As the weakly bound oxygen is extracted, the superconductivity is impaired and disappears completely if more than 0.03 a.u. of oxygen is lost. Since a rather small change in the oxygen content cannot cause such a strong degradation of the superconductor, the actual major role is probably played by the magnetic moment of stable nitroxyl radicals formed during HTMP oxidation (see below). In another study,[222] the $YBa_2Cu_3O_{7-x}$ ceramic was converted into a metastable state by mild removal of oxygen from the O(4) position (see Fig. 1 *b*) at 523 K using a different organic reducing agent, namely, azobenzene. The type of the kinetic dependence for oxygen removal from the Cu(1) layers allows one to assume that it involves the diffusion mechanism. The dynamics of the change in the crystal lattice parameters *a*, *b* and *c* depending on the oxygen concentration was followed. Subsequent treatment of the ceramic with iodine resulted in restoration of the lattice parameters to the original values (*i.e*. to those before the reaction with azobenzene).

Treatment of $YBa_2Cu_3O_{7-x}$ and $Bi_2Sr_2CaCu_2O_{8+x}$ with methanol [223] containing ~ 20 mass % of HTMP and 10% KOH as an HTMP oxidation catalyst [224] was also accompanied by extraction of weakly bound oxygen from the ceramics. The superconductivity parameters of the ceramics after this treatment strongly depended on their initial properties and on the methods of preparation. The superconductivity parameters of $YBa_2Cu_3O_{7-x}$ specimens obtained by cryochemical technology (A) and by self-propagating high-temperature synthesis (B) changed essentially upon contact with HTMP and KOH in methanol at 313 K for 120 min. The superconducting transition temperature of the specimen A decreased strongly (to 60 K). This was explained [223] by removal of reactive oxygen from the O(4) and O(5) positions of the $YBa_2Cu_3O_{7-x}$ crystal lattice. The specimen B displayed no trend to form a phase with $T_c = 60$ K, and the change in its superconducting transition temperature was smaller. This phenomenon is due to the specifics of structural transformations on the ceramic's surface, which hinder oxygen diffusion from the specimen bulk.[225, 226] These transformations were not observed in the oxygen extraction from the $Bi_2Sr_2CaCu_3O_{8+x}$ ceramic, and the superconductivity was suppressed completely. However, brief treatment with HTMP (15 min) increased the superconducting transition temperature by 13 K. It should be noted that a similar phenomenon was observed upon removal of a small amount of oxygen ($x \approx 0.03$) from the $Bi_2Sr_2CaCu_2O_{8+x}$ ceramic.[227–230] This is probably due to the extraction of the highly reactive oxygen intercalated between the BiO – OBi layers and the essential increase in the unit cell parameter *c*. Prolonged treatment

did not change T_c, but the fraction of the superconducting phase decreased to complete loss of superconductivity.

The much weaker effect of treatment with methanol containing 10% KOH on the specimen A than on the specimen B was explained by the higher oxidising and catalytic activity of the $YBa_2Cu_3O_{7-x}$ ceramic obtained by self-propagating high-temperature synthesis.[231] The extraction of oxygen from $Bi_2Sr_2CaCu_2O_{8+x}$ was accompanied by an insignificant decrease in the fraction of the superconducting phase and, as in the previous case, an increase in the superconducting transition temperature by 11 K. The difference between the effect of the 10% KOH solution in methanol and the effect of the HTMP solution in methanol is due to the fact that methanol cannot react with the weakly bound oxygen responsible for the material superconductivity.

In one of the first studies on the chemical modification of HTSC material surfaces,[232] various ferrocene derivatives containing aminoalkyl, aminoaryl, thiol, phosphino, amide and hydroxymethyl functional groups were adsorbed at room temperature onto the surfaces of the $YBa_2Cu_3O_{7-x}$ ceramic and thin film from a solution in acetonitrile. The solution concentration of the reagents was 10^{-3} mol litre^{-1}. It was shown by cyclic voltammetry that only molecules containing aminoalkyl, aminoaryl and thiol groups are adsorbed. This implies that preferential adsorption occurs on the $YBa_2Cu_3O_{7-x}$ surface. Ferrocenes containing such substituents as amide, phosphino and hydroxymethyl groups are virtually not adsorbed on HTSC materials. The pronounced ability of $YBa_2Cu_3O_{7-x}$ to adsorb amino groups is explained by the presence of the Cu(II) and Cu(III) ions on its surface. The adsorption of ferrocene derivatives with thiol groups is explained by the high oxidising ability of the superconducting material, on the one hand, and by the reducing properties of thiol groups, on the other hand. Treatment of thin $YBa_2Cu_3O_{7-x}$ film with solutions of various ferrocene derivatives in acetonitrile for 3 h at room temperature did not affect its superconductivity. An increase in the treatment time to 48 h decreased T_c by 2 K. It was noted that covering of the $YBa_2Cu_3O_{7-x}$ surface with a monolayer of molecules of substituted ferrocenes makes the HTSC material resistant against moisture.

Cyclic voltammetry was used to study the effect of small amounts of water on the adsorption of 11-mercaptoundecanoylferrocene (MUF) on the surface of the $Tl_{1.4}Ba_2CaCu_2O_z$ ceramic.[233] The presence of 5% water in a 0.1 M solution of MUF in acetonitrile decreased considerably the degree of coverage of the ceramic's surface with MUF molecules. If ethanol was used as the solvent, adsorption virtually did not occur. However, adsorption of MUF from dehydrated solvents gave a dense and stable monomolecular layer of chemisorbed MUF. It is believed that water affects adsorption due to a $BaCO_3$ layer formed as a result of corrosion, which does not adsorb MUF.

Direct proof of the chemical interaction between the amino groups and the $YBa_2Cu_3O_{7-x}$ surface was obtained in studies using Raman spectroscopy.[234] It was shown that 4-aminopyridine molecules are chemisorbed on the superconductor surface to form a dense monomolecular layer of vertically arranged molecules; the amino group is coordinated with the surface copper atoms of the superconductor (Fig. 7).

A small review of the early studies on the adsorption of organic molecules on HTSC materials[235] presented data on the chemisorption of ferrocenes containing various ligands, on the Raman spectra of monomolecular layers on HTSC material surface and on the kinetics of adsorbent–adsorbate exchange. Special attention was given to the practical use of HTSC materials modified with adsorbed organic molecules. For example, monolayer adsorption of hydrophobic molecules on HTSC materials can be used to prevent their corrosion in a humid atmosphere. In addition, this treatment increases considerably the adhesion between the polymer and the HTSC material. Superconductors coated with a monolayer of organic molecules can serve as the basis for obtaining synthetic tunnelling contacts used in superconducting quantum interferometer probes. They can also be useful for solving a number of fundamental problems of the physics of HTSC materials.

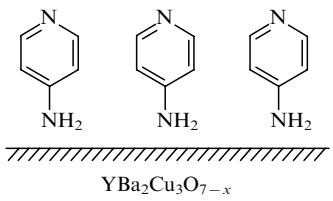


Figure 7. Coordination of adsorbed 4-aminopyridine molecules on the surface of the $YBa_2Cu_3O_{7-x}$ HTSC ceramic.[234]

Adsorption of naphthalene on the $YBa_2Cu_3O_{7-x}$ ceramic was accompanied by an increase in T_c and the transport critical current.[236] The treatment was carried out by immersion of samples in chloroform solutions of naphthalene of different concentrations. According to gravimetric data, this treatment results in covering of the surface of the samples with a shell of naphthalene molecules from one to several hundred monolayers thick. The transport critical current was measured with a vibrating magnetometer using a ring cut from the ceramic under study; the superconducting transition temperature was determined by recording the real part of magnetic susceptibility. Adsorption of naphthalene from 0.2 M solution in chloroform did not affect the critical superconductivity parameters of the specimen. An increase in the naphthalene concentration to 1 mol litre^{-1} increased the T_c by 1.5 K. Further increase in the naphthalene concentration did not change T_c considerably. For example, the T_c increase due to treatment of the specimen with a saturated solution (3.5 mol litre^{-1}) was 1.62 K. If naphthalene is washed off from the specimen with pure chloroform, the original superconducting transition temperature was restored almost completely (Fig. 8).

It has to be noted that the absolute value of the signal amplitude χ' did not depend on the treatment of the specimen. Hence, naphthalene adsorption does not change the fraction of the superconducting phase in the specimen. The transport critical current after naphthalene adsorption from a saturated solution increased by 20%. Additional experiments on measurements of the total current decay in a superconducting ring were carried out in order to analyse this interesting phenomenon. It was found that treatment of a specimen with naphthalene does not affect the decay rate and hence does not affect the pinning energy of the Josephson vortices.

The mechanism of the effect of adsorbed naphthalene on superconductivity has not been determined so far. Probably, a bond between an unoccupied *d* orbital of the Cu(III) ion in the superconductor and the molecular π orbital of naphthalene is

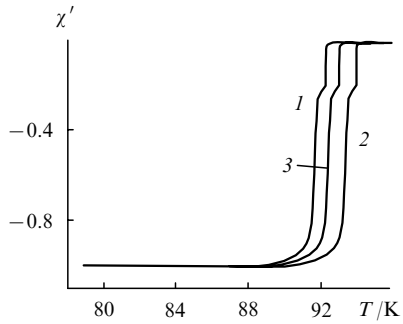


Figure 8. Temperature dependence of the real part (χ') of magnetic susceptibility of the $YBa_2Cu_3O_{7-x}$ ceramic;[236] (*1*) original specimen; (*2*) after treatment with saturated solution of naphthalene in chloroform; (*3*) after washing the treated specimen with pure chloroform.

formed, which favours electron transfer to the superconductor and hence changes its properties.

The change in the superconducting transition temperature caused by the naphthalene adsorption cannot be explained by donor-acceptor interactions, since interactions of electron donors with superconductors having hole-type conductivity most probably decrease the concentration of the charge carriers and hence decrease rather than increase T_c. The increase in T_c observed in the experiment is probably determined by the effective charging of the superconductor granule surfaces upon adsorption of naphthalene molecules.[237]

As shown above, the effect of adsorption of organic molecules on the properties of HTSC materials primarily results from donor-acceptor interactions or redox reactions involving copper and oxygen ions. On the other hand, the high sensitivity of the critical parameters of superconductivity to external magnetic field provides a reason to assume that the superconductor properties are strongly affected by paramagnetic species, *i.e.*, radicals possessing magnetic moments.

The effect of adsorption of a stable nitroxyl radical, 2,2,6,6-tetramethylpiperidin-*N*-oxyl (TEMPO), on the transport properties of the $YBa_2Cu_3O_{7-x}$ superconducting ceramic was studied.[238, 239] Adsorption was carried out at room temperature by immersing the ceramics in a 0.2–2.0 M chloroform solution of TEMPO. The specimen was kept in the solution for 12 h and dried in air. The critical current was measured as a function of temperature using a vibrating magnetometer. In reference experiments, the specimens kept in pure chloroform for 30 days did not show any effect of chloroform on the ceramic's properties. The superconducting transition temperature was measured by recording the magnetic susceptibility on an alternating current magnetometer. Figure 9 shows the dependences of the transport current I_c on temperature at various radical concentrations in the starting solution. It is evident that radical adsorption affects rather strongly the critical current in the temperature range from 77.4 to 86 K. At a content of adsorbed radicals in the ceramic equal to 1.7×10^{-2} mass %, the critical current was higher than that in the original non-treated specimen over the entire temperature range studied. Further increase in the content of radicals decreased I_c (see Fig. 9). The superconducting transition temperature of the ceramic before and after adsorption of radicals remained the same.

The mechanism of the effect of adsorbed molecules with their own magnetic moments on superconductivity is probably rather complicated. The results of additional experiments carried out specially to reveal the characteristic features of this effect were analysed within the framework of the intergranular conductivity

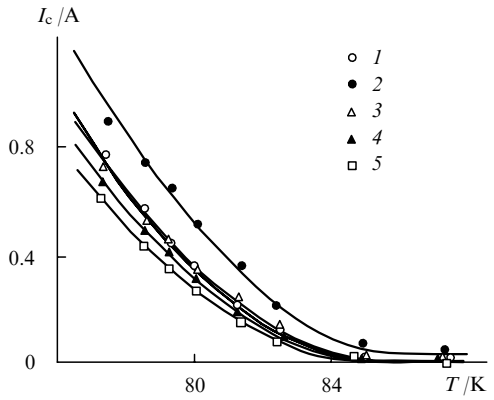


Figure 9. Temperature dependence of the critical current in the $TEMPO_y$–$YBa_2Cu_3O_{7-x}$ composite material at the following concentrations of the stable radical: 0 mass % (*1*), 1.7×10^{-2} mass % (*2*), 4.2×10^{-2} mass % (*3*), 8.5×10^{-2} mass % (*4*), 1.7×10^{-1} mass % (*5*).[238, 239]

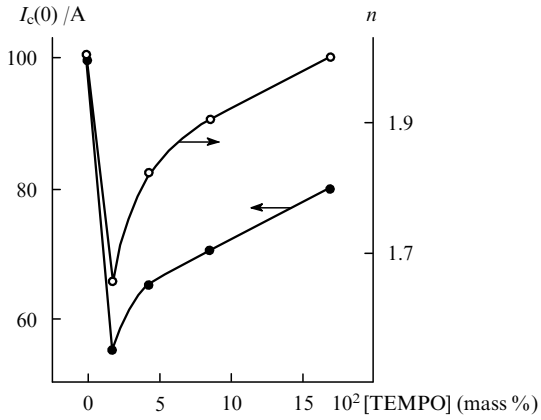


Figure 10. Dependence of the critical current extrapolated to 0 K and the exponent n in the Eqn (3) on the concentration of stable radicals TEMPO in the $YBa_2Cu_3O_{7-x}$ ceramic.[238, 239]

model.[240] The general temperature dependence of the critical current for various contacts between the granules has the form

$$I_c(T) = I_c(0)\left(1 - \frac{T}{T_c}\right)^n, \qquad (3)$$

where $I_c(0)$ is the critical current obtained by extrapolation to 0 K; n is an index reflecting the nature of contacts between the granules, which can vary from 1 to 2. Figure 10 presents the calculated dependences of the critical current $I_c(0)$ and the index n on the concentration of radicals.[238, 239] It is evident that n is equal to 2 in the absence of radicals and $n < 2$ at their low concentrations. This means that upon adsorption of a radical, an SNS contact is transformed to an SNINS contact, or, in other words, the intergranular bond is improved and approaches a character close to the classical Josephson transition.[240] On the other hand, the absolute value of the critical current also decreases, apparently due to the effect of the radical magnetic field on the intergranular bond. If the radical concentration is increased further, n eventually becomes equal to two. The change in the intergranular conductivity correlates with the change in the critical current $I_c(0)$. The increase in the latter at high radical concentrations is probably due to a specific behaviour of the highly concentrated magnetic media. For example, it is known that at a concentration of paramagnetic species above a certain value a significant change in the spin orientation is observed and the total magnetic moment of the medium decreases. Hence, in our case the increase in the concentration of stable radicals should weaken the effect of the magnetic moments on the conductivity of the intergranular layer, which is confirmed experimentally.

A study of the transport properties of the $YBa_2Cu_3O_{7-x}$ HTSC ceramic upon magnetic field trapping by granules of the specimen showed that an increase in the critical current between the granules is actually observed at certain parameters of the magnetic field 'uptaken' by the granules.[242] Moreover, treatment of a superconducting ceramic ring with stable radicals does not change the decay rate of the current induced in the ring. Hence, additional pinning centres are not formed, and probably the increase in the transport critical current in the $YBa_2Cu_3O_{7-x}$ ceramic after adsorption of stable radicals mostly occurs due to 'uptake' of magnetic field of a radical in the specimen granules. It was shown experimentally[241] that interaction of the Josephson and Abrikosov vortices can increase the critical current essentially. An effect on the intergranular bonding and the donor-acceptor properties of the stable radical, which probably manifests itself as a change in the index n in Eqn (3), cannot be ruled out either. However, the major role still belongs to the 'uptake' of the radical magnetic field into the specimen granules.

The critical parameters of superconductivity of the $YBa_2Cu_3O_{7-x}$ ceramic containing adsorbed radicals depend on

the temperature to which a specimen has been cooled prior to the measurements.[243] The type of the temperature dependence of magnetic susceptibility indicates an increase in the critical parameters of superconductivity upon cooling of the specimen. The explanation for this is that at lower temperatures, greater magnetic flux from the radical molecules is 'uptaken' by the granules, resulting in an increase in the critical parameters.

The effect of the adsorption of a stable diphenylpicrylhydrazyl radical (DPPH) on the superconductivity of the $Bi_{1.8}Pb_{0.5}Sr_{1.9}Ca_{2.5}Cu_{3.2}O_z$ ceramic was studied.[244] Before an experiment, the surface of the specimen to be studied was freed from adsorbed water, CO_2 and organic contaminants by calcination in an oven at 473 K *in vacuo* for one hour. Then the cleaned specimen was transferred into a glass tube containing DPPH powder and sealed. The adsorption of DPPH was carried out by heating the tube to 473 K for 20 min. After that, the tube was broken, and the specimen was transferred into a cell for measurement of magnetic properties. For reference purposes, the procedure described above was also carried out in the absence of DPPH. The superconductivity parameters of the specimen under study were measured with an alternating current magnetometer. Figure 11 presents the temperature dependence of the magnetic susceptibility of the $Bi_{1.8}Pb_{0.5}Sr_{1.9}Ca_{2.5}Cu_{3.2}O_z$ ceramic. It is evident that upon adsorption of the radical, the curve shifts towards the low-temperature region; this indicates that the current-carrying ability of the specimen decreases. Thermal treatment of the ceramic also deteriorates superconductivity, but in this case the change is much less. The experimental values of magnetic susceptibility were compared with the real part of the magnetic susceptibility calculated within the framework of the simple Kim model.[245] Good agreement between the experimental results and the calculations were achieved with the assumption that the intergranular layer is affected by a static magnetic field of 0.13 mT (see Fig. 11, curve *2*).

Given the magnetic induction B, one can estimate the distance d between an adsorbed radical molecule and an intergranular contact:

$$d = \left(\frac{2\mu}{B}\right)^{1/3}, \qquad (4)$$

where $\mu = g\beta S$ is the magnetic moment of the radical, $g = 2$ is the g-factor of a free electron, β is the Bohr magneton, $S = 1/2$ is the spin quantum number. Substituting the above value of $B = 0.13$ mT in the formula (4), we obtain $d = 5.6$ nm. This distance is in good agreement with the thickness of the non-superconducting layer, which is generally located on the superconductor surface and is estimated as 3–5 nm.[246] Such consistency supports the suggested model of the effect of the magnetic field of adsorbed radicals on the intergranular current in superconducting ceramics.

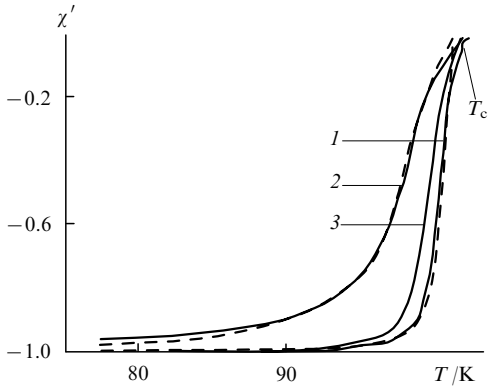


Figure 11. Temperature dependence of magnetic susceptibility of the $Bi_{1.8}Pb_{0.5}Sr_{1.9}Ca_{2.5}Cu_{3.2}O_z$ ceramic;[244] (*1*) original specimen; (*2*) after adsorption of the DPPH radical; (*3*) after heating in a sealed tube for 1 h. Solid lines — experiment, dashed lines — calculated real part of magnetic susceptibility within the simple Kim model.

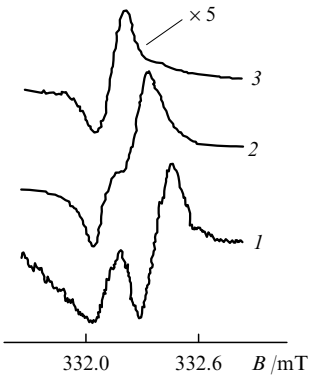


Figure 12. EPR spectra of the DPPH radical adsorbed on the surface of the $Bi_{1.8}Pb_{0.5}Sr_{1.9}Ca_{2.5}Cu_{3.2}O_z$ superconducting ceramic recorded at the temperatures: 77.4 (*1*), 89 (*2*) and 125 K (*3*).[244]

The EPR spectrum of the DPPH radical adsorbed on the surface of the $Bi_{1.8}Pb_{0.5}Sr_{1.9}Ca_{2.5}Cu_{3.2}O_z$ ceramic in superconducting state at 77.4 K consists of two lines (Fig. 12). As the specimen is heated, the high-field line of the doublet starts to shift downfield and, since the position of the low field line remains unchanged, splitting decreases. At 125 K, *i.e.*, at a temperature above T_c, the high-field line coalesces with the low-field one, and a singlet corresponding to the line in the EPR spectrum of the DPPH radical remains. It follows that the low-field line of the doublet, the position of which is not changed, corresponds to the adsorbed radical located at a great distance from the superconducting phase. For this reason, this phase does not affect the low-field line. The shift of the high-field line with the increase in temperature can be caused by the following reasons. First, the magnetic flux trapped by granules of a superconducting specimen (the Abrikosov vortices) located in an external magnetic field with $B_0 \approx 0.33$ mT changes the magnetic field parameters in the vicinity of the adsorbed radical. Second, the magnetic moment of the adsorbed radical has a 'mirror' image in the diamagnetic surface of the superconducting specimen, and probably the line position in the EPR spectrum of the radical is actually determined by the magnetic field of this 'mirror' dipole.

2. Intercalation of organic molecules into the crystal structure of high-temperature superconducting materials

A characteristic feature of HTSC materials is their layered structure which plays an important role in the transition to the superconducting state. As noted above and as has been shown by Bulaevskii,[247] intercalation of atoms and molecules into the structure of layered solids changes essentially their chemical and physical properties. For example, intercalation of pyridine molecules into the TaS_2 superconductor was accompanied by a significant increase in the superconducting transition temperature (from 0.5 to 4.5 K).[248] Hence, one can expect that intercalation of organic molecules in an HTSC material would affect strongly the critical parameters of superconductivity. It was even suggested that intercalation of organic molecules in layered inorganic materials can result in superconductors with high critical temperatures.[249]

Bismuth oxide- and thallium oxide-containing superconductors can be suitable objects for studying the effect of intercalation on superconductivity. In fact, the magnetic properties of the $Bi_{1.7}Pb_{0.3}Sr_2Ca_2Cu_3O_z$ ceramic with $T_c = 105$ K underwent interesting changes on treatment with benzene.[250] A powder with a particle size of ~ 50 μm obtained by grinding bulk ceramic specimens was placed in benzene and kept at room temperature for a period from 10 min to 2.5 h. Then benzene was evaporated at 308 K, and the powder was placed in molten paraffin in order to

prevent electrical contact between the granules. As a rule, the specimens obtained by this method manifested weak paramagnetism with an absolute susceptibility of 10^{-7} or ferromagnetism with a magnetisation of 10^{-9} A m^2 g^{-1}.

Specimens of the ceramic that had been kept in benzene for 20–30 min had unusual electrophysical properties. First, rather high diamagnetic response was recorded at room temperature and hysteresis phenomena were observed in low magnetic fields. For example, the magnetisation in a field of 10 mT at 300 K was 8×10^{-6} A m^2 g^{-1}. Second, a stepwise change in the external magnetic field was accompanied by magnetisation relaxation. Third, if the temperature of the specimen was cycled in the range from 77.4 to 300 K, the initial magnetisation decreased gradually. For example, the maximum magnetisation of a specimen was 2×10^{-5} A m^2 g^{-1} after the first cooling, whereas it was as low as 8×10^{-6} and 4×10^{-6} A m^2 g^{-1}, respectively, after the second and third cooling. Fourth, the EPR spectrum of the specimen at 300 K contained a low-field microwave absorption signal. Repeated cyclic changing of the specimen temperature decreased this signal. X-Ray diffraction analysis revealed additional reflections, apparently due to a new phase that was formed in the specimen. Such unusual physical properties of the $Bi_{1.7}Pb_{0.3}Sr_2Ca_2Cu_3O_z$ ceramic containing intercalated benzene can be a manifestation of superconductivity. Therefore, the authors of this study [250] believed that they could detect a small fraction of a superconducting phase in a specimen at room temperature. Unfortunately, the phenomena described above were only observed on some specimens. They could not be reproduced in other specimens, and the fraction of the superconducting phase could not be increased by varying the treatment conditions.

Later, a detailed study of the intercalation of planar aromatic molecules into superconducting ceramics was undertaken.[251] Intercalation of benzene and phthalocyanine complexes of copper and nickel into bismuth-containing ceramics, $Bi_2Sr_2CaCu_2O_z$ and $Bi_2Sr_2Ca_2Cu_3O_z$, and into a thallium-containing ceramic, $Tl_2Ca_2BaCu_2O_z$, were carried out in sealed tubes at 273–423 K. As in yet another study,[250] the ceramics studied displayed unusual physical properties at room temperature: the specimens retained magnetisation for some time after the external magnetic field was turned off; a low-field microwave absorption signal was observed; the magnetisation curves had unusual shapes; negative magnetisation was recorded in low magnetic fields (1–2 mT). X-Ray diffraction and Raman spectroscopic data showed that these organic compounds were located between the Tl—O or Bi—O double layers (see Fig. 1 *c*).

Intercalation of zinc and nickel phthalocyanine complexes also affected the properties of bismuth- and thallium-containing HTSC ceramics. In Ref. 252, as in previous studies,[250, 251] unusual physical properties of these ceramics at room temperature were reported. For example, at 300 K the magnetisation of a metal phthalocyanine intercalated in the ceramics was found to be anomalously high, two orders of magnitude higher than the magnetisation of a free metal phthalocyanine complex. In the superconducting state (at 90 K), the magnetisation of the ceramics with the intercalated complex was one order of magnitude smaller and was equal to 10^{-2} A m^2 g^{-1}. The temperature dependence plots of the magnetisation of $(NiPc)_{0.1}Bi_2Sr_2CaCu_2O_z$ and $(NiPc)_{0.09}Tl_2Ca_2BaCu_2O_z$ specimens (Pc = $C_{32}H_{16}N_8$) obtained on cooling in magnetic fields and without a field showed noticeable differences starting from 250 K. Such unusual magnetic properties can indicate that the specimens display superconductivity at rather high temperatures. Certain assumptions on the nature of the observed phenomena were made.[250–252] It was assumed that molecules of aromatic compounds characterised by strong electron delocalisation form new composite materials when introduced into the structure of a layered superconductor. These materials manifest unusual physical properties which resemble in certain respects the properties of superconductors; this is primarily due to the possible formation of quasi-species — 'anyons' with half-integer statistics. It was shown theoretically [253] that similar quasi-species present in two-dimensional electronic systems can generate a superconducting state, the transition to which occurs by a mechanism different from the generally accepted one and which is characterised by a higher T_c.

In addition, the superconductivity of intercalated composites can be explained using the exciton mechanism.[254] In fact, intercalation of organic molecules into layered crystal systems results in 'sandwiches' that consist of alternating thin metal layers and dielectric intermediate layers. An electron–hole pair (exciton) can be formed in such systems. High magnetisation of intercalated bismuth- and thallium-containing HTSC oxides can also be due to the joint orbital contribution of π-electrons of aromatic molecules, which can form two-dimensional conducting layers due to the structural features of the material. According to X-ray diffraction data,[252] intercalation changes the material structure substantially. Not only do the distances between the structural Tl—O and Bi—O layers change, but also those between the atoms along the *a* and *b* axes (see Fig. 1 *c*). These transformations affect the electronic condition of the copper ion and result in transition from the usual phase with antiferromagnetic ordering of the copper spin states to the ferromagnetic phase. The effect of the amount of the metal phthalocyanine intercalated in the ceramics on this process was observed for the $(NiPc)_yBi_2Sr_2CaCu_2O_z$ system.[252]

V. The effect of superconductivity on the electronic state of the adsorbed molecules and on adsorption processes

The effect of the substrate superconductivity on the fluorescence lifetime of an adsorbed dye, 1,4-bis(5-phenyloxazol-2-yl)benzene (POPOP), was studied.[255] Adsorption of the dye on a $YBa_2Cu_3O_{7-x}$ ceramic substrate was carried out by treating the specimen with a 10^{-3} M POPOP solution for 100 s in toluene followed by drying in air. As a result of this treatment, the width of the superconducting transition temperature of the substrate, $\Delta T = 1$ K, expanded to $\Delta T = 8$ K towards low temperatures. The fluorescence lifetime τ at each particular temperature was calculated using an exponential kinetic curve of the decay of the dye fluorescence excited by light with a wavelength of $\lambda = 330$ nm. Figure 13 presents the temperature dependences of the relative specific resistance of the substrate (ρ/ρ_{298}, where $\rho_{298} = 2\times10^{-3}$ Ω cm is the substrate specific resistance at 298 K) and the lifetime of fluorescence of adsorbed POPOP (τ). If temperature is decreased, an abrupt increase in τ is observed in the region of transition into the superconducting state. In control experiments, where the fluorescence lifetime of POPOP molecules adsorbed on a non-superconducting substrate with similar com-

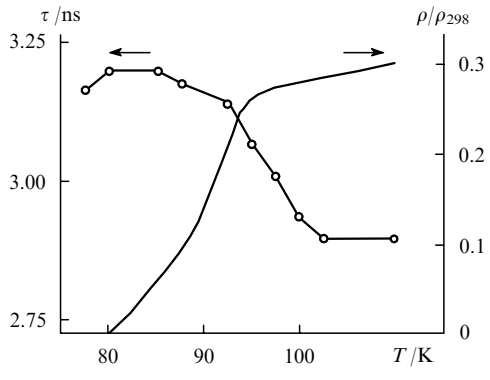


Figure 13. Temperature dependences of the relative specific resistance of the $YBa_2Cu_3O_{7-x}$ support and the fluorescence lifetime of POPOP adsorbed on this support.[255]

position was measured, no such dependence of τ on temperature was observed.

Thus, the abrupt increase in the lifetime of the electronically excited singlet state of POPOP upon temperature decrease is due to the specific features of the superconducting state of the substrate. Probably, the following aspects are most important. First, the transition of the ceramic in the superconducting state is accompanied by small structural changes of its crystal lattice,[256, 257] which can affect the geometry of the adsorbed molecule and thus change the lifetime of the excited electronic state. Second, the transition into the superconducting state changes the dielectric constant of the surface layer of the HTSC material;[258] this results in a change in the electric field strength near the surface and hence can affect the probability of nonradiative transitions of the excited molecules of the adsorbate. Third, the transition of the substrate in the superconducting state can weaken the interaction of the electronically excited adsorbate molecule with the conductivity electrons of the substrate, which also affects the luminescence lifetimes.

The effect of the substrate superconductivity on the electronic state of the adsorbed molecule was observed:[258] the fluorescence quantum yield of an organic dye, erythrosine, adsorbed on a superconductor surface changed in a stepwise manner at the superconducting transition temperature of the substrate. A bulk ceramic specimen of $YBa_2Cu_3O_{7-x}$ (T_c = 87 K), an epitaxial polycrystalline film of $YBa_2Cu_3O_{7-x}$ (T_c = 50 K) and a low-temperature superconductor film of NdN (T_c = 13.5 K) were used as the superconductors. The fluorescence quantum yield of erythrosine applied on the low-temperature superconductor NdN underwent a small (5%) stepwise change at T_c, while the quantum yield above and below this point virtually did not depend on temperature. A different behaviour was observed where the dye was adsorbed on HTSC substrates. The fluorescence quantum yield of erythrosine adsorbed on a $YBa_2Cu_3O_{7-x}$ polycrystalline film increased by 100% as the latter has passed in the superconducting state. The quantum yield of erythrosine adsorbed on the bulk $YBa_2Cu_3O_{7-x}$ ceramic changed substantially around the temperatures of 50 and 90 K, which correspond to two superconducting subsystems, *viz*., the intergranular layers and granules, respectively. The conclusion was made [258] that the fluorescence quantum yield of the dye changes upon transition of the adsorbate in the superconducting state owing to the change in the dielectric constant of the material.

An original way for the separation of diamagnetic and paramagnetic molecules on a porous membrane made of a superconducting material, $YBa_2Cu_3O_{7-x}$, was reported.[259] In the superconducting state, the porous ceramic is 'transparent' for nitrogen molecules but does not pass the paramagnetic molecules of oxygen. The $O_2 : N_2$ concentration ratio decreased by a factor of six after a gas mixture (air) has passed through such a membrane. There was no gas separation effect with a non-superconducting membrane at the same temperatures, which is explained by high (comparable with the energy of thermal movement of molecules) energy of interaction between the magnetic moment of a triplet oxygen molecule and its mirror image in the superconducting surface of the membrane material. As a result, the effective cross-section of interaction of the oxygen molecule with the superconductor increases and a paramagnetic oxygen molecule penetrates the membrane with greater difficulty than a diamagnetic nitrogen molecule.

The features of interaction of HTSC materials with charged or magnetoactive species provide the possibility of using these materials for practical purposes. For example, the focusing of electron and ion beams passing through a superconducting tube made of HTSC ceramics was identified and studied.[260–262] A theoretical estimate [260] of the focusing effect of a superconducting surface on the beam of free electrons or ions showed that at certain velocities of the beam the focusing force can be comparable to, or even exceed, the force of Coulomb repulsion of the charged species in the beam. The vast experimental and theoretical material that has been accumulated shows the possibility of using HTSC materials for these purposes.[261] For example, the passage of an electron beam through a superconducting tube from bismuth-containing ceramics with T_c = 105 K was studied experimentally:[262] an electron beam with an energy of 340 keV, an intensity of 0.8 kA and a diameter of 8 mm was directed into a superconducting tube. The electron beam leaving the tube was focused to a diameter of 1.1 mm.

The authors of the present review have thoroughly studied the interaction of a superconductor with magnetoactive species.[263, 264] Specific features of the low-temperature adsorption and desorption of oxygen and argon on a 0.25–0.50 mm fraction of powder of the $YBa_2Cu_3O_{7-x}$ superconducting ceramic were studied. The adsorption isotherms of argon and oxygen in the temperature range from 77.4 to 98 K were obtained.

The desorption curves coincided completely with the adsorption curves. Hence, the adsorption of argon and oxygen on the oxide $YBa_2Cu_3O_{7-x}$ is reversible and can be regarded as physical adsorption. The experimental isotherms of the argon and oxygen adsorption in the entire temperature range studied correspond to the 'second type' [265] and are well described by the BET polymolecular adsorption theory.[266] The temperature dependence of the superconducting adsorbent specific surface calculated using the BET equation for oxygen adsorption differs essentially from the similar dependence obtained for argon adsorption (Fig. 14). According to the BET theory, the geometrical dimensions of the surface do not depend on temperature and are determined by the nature of the material. This assumption is totally consistent with the low-temperature adsorption of argon. The specific surface of the specimen measured with respect to argon was found to be 1.05 $m^2\ g^{-1}$.

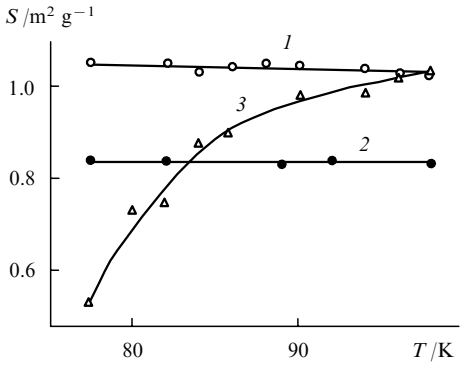


Figure 14. Temperature dependences of the specific surface measured by the BET technique from adsorption of Ar (*1*) and O_2 (*2*, *3*) on the $YBa_2Cu_3O_{7-x}$ adsorbent in superconducting (*1*, *3*) and non-superconducting states (*2*).[263]

A different situation is observed for the adsorption of paramagnetic oxygen molecules. At 77.4 K where the adsorbent is in the superconducting state, the amount of oxygen adsorbed in a monolayer is more than twice as small as that in the case of argon. As temperature increases, the amount of adsorbed oxygen increases, and when the adsorbent is no longer in the superconducting state, oxygen is adsorbed exactly in the same way as diamagnetic argon (see Fig. 14). Adsorption of oxygen on a non-superconducting adsorbent prepared by heating the original superconducting adsorbent in air to 873 K followed by quenching to room temperature was studied for reference purposes. In this case, the specific surface does not depend on temperature, and its small decrease in comparison with the specific surface of the original superconducting adsorbent is apparently due to partial sintering of small granules during thermal treatment of the ceramic at 873 K.

The anomaly observed in the low-temperature adsorption of molecular oxygen on HTSC ceramics is undoubtedly due to the

paramagnetism of O_2 molecules and the superconducting state of the adsorbent. It is believed [259] that perfect diamagnetism of the adsorbent in the superconducting state favours its additional interaction with the paramagnetic oxygen molecule. However, estimates show that the energy of repulsion between the magnetic moment of oxygen and its mirror image in the superconducting adsorbent can be comparable with the energy of thermal movement only at distances equal to the molecular diameter. This does not consider the London penetration depth of magnetic field into the superconductor and the thickness of the possible non-superconducting phase layer on the adsorbent surface. A more reasonable assumption is that the repulsive force arises due to the interaction between the magnetic moment and the magnetic flux 'uptaken' by the granules of the superconducting adsorbent.[267]

As the temperature is increased, the adsorbent diamagnetism decreases and the amount of adsorbed oxygen increases synchronously, tending to a limit which corresponds to complete surface coverage. Measurements of the 'pure' heat of adsorption

$$Q_a = q_{st} - q_L ,$$

(where q_{st} is the isosteric heat of adsorption and q_L is the heat of condensation of the adsorbate on a planar surface) also indicate a significant difference between the adsorption of molecular oxygen on superconducting and non-superconducting adsorbents. As the surface of a non-superconducting adsorbent is covered with oxygen, Q_a decreases monotonically (Fig. 15). This agrees with the common concept of adsorption on non-porous solids with the 'classical' non-uniform surface. Conversely, Q_a increases in the case of oxygen adsorption on superconducting adsorbents. This can be a consequence of the formation of new adsorption sites as the surface is covered with oxygen molecules due to violation of superconductivity in the near-surface zone by the strong magnetic field of the adsorbed molecules.

In continuation of previous works,[263, 264] the heat transfer from a heater to a superconductor by argon, nitrogen, helium and oxygen molecules was studied.[268] It is well known that the heat transfer from gas to solid occurs efficiently only in the case if the collision of the gas molecules with the surface is inelastic. Therefore, based on the above data on the adsorption of paramagnetic molecules,[112, 263] it can be assumed that oxygen transfers heat to a superconductor less efficiently than molecules which have no magnetic moment. The efficiency of heat transfer by gas molecules to the surface of the $YBa_2Cu_3O_{7-x}$ superconducting ceramic was estimated as the time required for heating the specimen to T_c. Specimens of the $YBa_2Cu_3O_{7-x}$ ceramic had different critical parameters: the specimen Y1 was characterised by a large strength of the first critical magnetic field of the granules $H_{c1g} = 1.02 \times 10^4$ A m^{-1} and $T_c = 89.1$ K, while the specimen Y2 had the following parameters: $H_{c1g} = 1.4 \times 10^3$ A m^{-1} and $T_c = 91.3$ K. The electron micrographs of the cross-sections of specimens Y1 and Y2 taken with a scanning electron microscope showed that their morphologies differ essentially: the specimen Y1 consists of distinct oriented monolithic blocks with characteristic cross sizes of $\sim 40 \times 100$ μm, whereas the specimen Y2 consists of randomly oriented granules with an average size of ~ 10 μm.

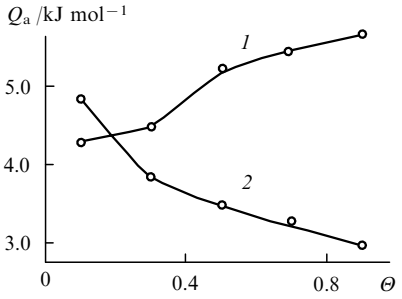


Figure 15. Dependence of the 'pure' heat of adsorption (Q_a) of oxygen on the $YBa_2Cu_3O_{7-x}$ ceramic in superconducting (*1*) and non-superconducting (*2*) state on the degree of surface coverage (Θ) with molecular oxygen in the temperature range of 77.4–96 K.[263]

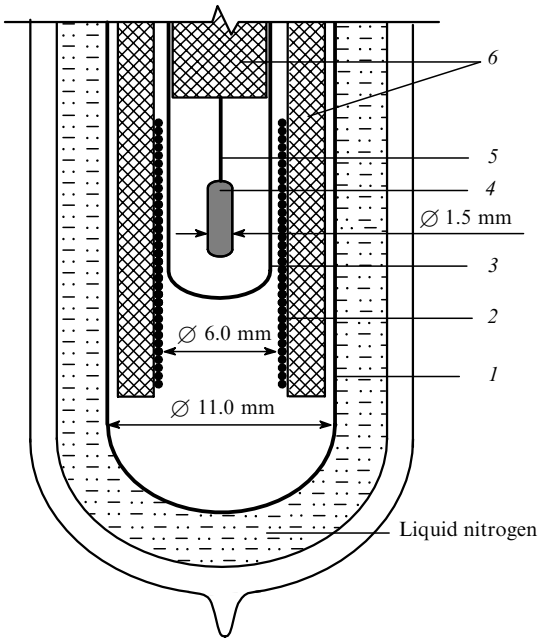


Figure 16. Scheme of measuring cell for recording the heating rate of HTSC materials in nitrogen or oxygen media;[268] (*1*) external glass flask of the measuring cell; (*2*) heater; (*3*) quartz tube; (*4*) specimen; (*5*) capron thread; (*6*) thermal insulation.

The period from the moment when the heater has been turned on to the moment when the ceramic passes into the normal state was measured in different gaseous media in a cell (Fig. 16) placed in a mutual inductance coil for recording the magnetic susceptibility of the specimens. Figure 17 shows the experimental depend-

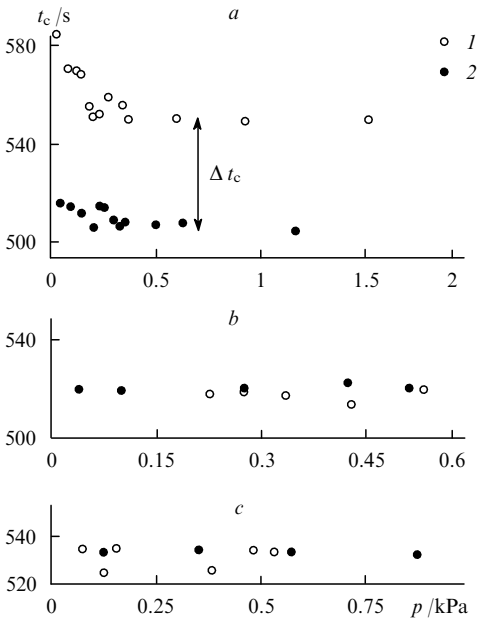


Figure 17. Dependence of the time required for heating a specimen to the superconducting transition temperature on the pressure of oxygen (*1*) and nitrogen (*2*) in the measuring cell;[268] (*a*) measurements on the Y1 specimen; (*b*) measurements on the Y1 specimen coated with a paraffin film; (*c*) measurements on the Y2 specimen.

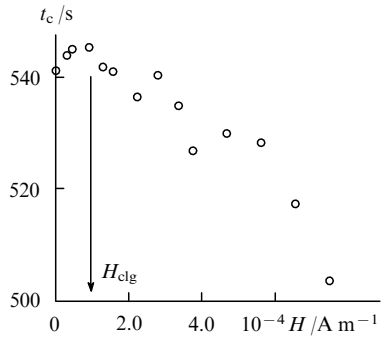


Figure 18. Dependence of the time of the Y1 specimen heating to the temperature of superconductivity loss on the external magnetic field strength.[268]

ences of time (t_c) required for heating the specimen to the superconducting transition temperature in a nitrogen or oxygen atmosphere on the pressure of these gases in the measuring cell. When the specimen Y1 was heated in oxygen, the time t_c was obviously greater than that in nitrogen. On the specimen Y2 and on the specimen Y1 coated with a paraffin film, the time t_c did not depend on the atmosphere in which heating was carried out. In addition, the time of heating of the specimen Y1 in oxygen depended on the strength of external magnetic field imposed on the specimen after cooling (Fig. 18). The time t_c remained unchanged if the strength of the external magnetic field did not exceed H_{c1g} for the particular specimen. Further increase in field strength resulted in a decrease in t_c. Based on these experiments, it can be concluded that heat transfer by oxygen molecules to a superconducting specimen with high critical parameters occurs with lower efficiency.

The essential difference of the oxygen molecule from the nitrogen molecule is its magnetic moment, therefore it can be believed that its interaction with the superconductor is responsible for the observed phenomenon. As shown above,[263] the magnetic moment of oxygen can favour the decrease in its adsorption on the superconductor surface. Apparently, in this case the oxygen molecules transfer heat less efficiently because they are elastically reflected from the superconductor surface. Taking into account that the character of collisions of oxygen molecules with a superconductor surface depends on its critical parameters, it is possible to suggest a new model of the interaction of the magnetic moment of oxygen with superconductors. In contrast to the previously suggested model of interaction between the magnetic moment and the Meissner superconductor phase,[259] it is assumed [267, 269] that the repulsive force of the magnetic moment from the superconductor surface is described by the power function

$$F \propto d^{-n},$$

where the index n depends on the distance d between the magnet creating the magnetic field and the superconductor. At long distances and in the cases where the magnetic field strength of the magnet does not exceed the first critical field strength of the superconductor, $n = 4$; this corresponds to the ordinary dipole–dipole interaction. At short distances, *i.e.*, in sufficiently strong magnetic fields, the character of interaction of the magnet with the superconductor changes substantially. The magnetic field of the magnet penetrates into the superconductor bulk; as a result, the superconductor passes into a mixed state. In this case, interaction is described by the vortical model, according to which the magnetic flux from the magnet is 'uptaken' by the bulk of the granules, creating a grid of vortical lines reaching the superconductor surface and capable of interacting with the magnet. The interaction energy is expressed by the formula [270]

$$E = \frac{mH_{clg}\delta}{\pi d}, \qquad (5)$$

where m is the magnetic moment and δ is the superconductor thickness. It should be noted that in this case the energy of interaction depends on distance much more weakly than in the Meissner model (d^{-1} instead of d^{-3}).

According to the estimate made, the energy of interaction between the magnetic moment of oxygen and the surface of the specimen Y1 is rather high and is comparable with the thermal energy kT at a distance $d \approx 5$ nm. This distance is much larger than the oxygen molecule size and the thickness of the possible non-superconducting phases usually present on HTSC surfaces. The energy of interaction with the surface of the specimen Y2 becomes equal to the thermal energy kT only at $d \approx 0.05$ nm, which is less than the oxygen molecule size, hence repulsion does not occur in this case. This agrees with the experimental results mentioned above.

Thus, superconductivity affects the adsorption and collision of paramagnetic molecules with the superconductor surface.[263, 264, 268] It is important that these processes are also controlled by the external magnetic field.[271]

Heterogeneous chemical reactions are very 'sensitive' to the state of the surface. The recoil force, which appears during desorption of hydrogen molecules which acquire nonequilibrium translational energy upon their recombination at the surface was measured after keeping a $YBa_2Cu_3O_{7-x}$ superconductor in a stream of hydrogen atoms.[272] The measurements were carried out by the weighing method in the temperature range of 78–350 K. The recoil force did not depend on temperature as long as the superconductor was in the ordinary state. After its transition to the superconducting state, a decrease in the recoil force was recorded. This was explained by a change in the magnetic state of the surface. The temperature dependence of the recoil force correlates well with changes in the relative intensity of the ferromagnetic resonance absorption of the superconductor. This correlation suggests that the recombination of hydrogen atoms occurs at the antiferromagnetically ordered Cu^+ surface ions. Cooling of the substrate changes the magnetic ordering and hence affects the concentration of the Cu^+ ions at the surface. The decrease in the recoil force below the superconducting transition temperature of the substrate is apparently due to magnetic shielding of the Cu^+ ions due to of the total diamagnetism of the superconductor.

The low-temperature catalytic reaction of the *ortho–para* conversion of molecular hydrogen on the superconducting catalyst $YBa_2Cu_3O_{7-x}$ was studied.[273, 274] The catalytic activity of the superconductor at various temperatures was estimated by chromatographic measurement of the amplitude of *para*-hydrogen signal on exit from the reactor. The temperature dependence of the effective rate constant of catalytic *ortho–para* conversion is

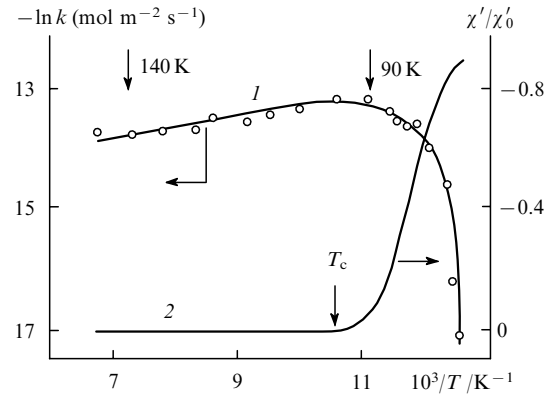


Figure 19. Temperature dependences of the effective rate constant of the *ortho–para* hydrogen conversion on the superconducting catalyst $YBa_2Cu_3O_{7-x}$ (*1*) and the real part of the relative magnetic susceptibility of this catalyst (*2*).[273]

presented in Fig. 19. One can see that the conversion rate decreases abruptly starting from 90 K. This temperature is close to the superconducting transition temperature of the catalyst determined from magnetic susceptibility (see Fig. 19, curve *2*). Analysis of the possible magnetic mechanisms of hydrogen *ortho–para* conversion on oxide catalysts [275–278] made it possible to conclude that the magnetic state of the catalyst's surface plays an important role in these processes. Before a catalyst is transferred to the superconducting state, *ortho–para* conversion of hydrogen occurs on the paramagnetic centres; the Cu^{2+} cations play this role in HTSC materials. Superconductivity changes essentially the magnetic state of the catalyst and it acquires a new property, *i.e.*, becomes a pure diamagnetic. The currents flowing along the surface shield the magnetic field of the paramagnetic centres and thus 'switch off' the basic mechanism of the low-temperature catalytic *ortho–para* conversion. As a result, the effective reaction rate constant decreases by several orders of magnitude.

VI. Conclusion

Analysis of the experimental and theoretical data presented above shows that the specific features of interaction of external molecules with HTSC materials are determined by a wide range of various physicochemical processes. The thermodynamic metastability of almost all of the known high-temperature superconductors [60, 279, 280] probably has certain impact on the processes involved in the synthesis of HTSC materials and on the effects of external molecules on these processes. The study of superconductivity in HTSC materials requires rather complex problems to be solved. Of these, the reproducible synthesis and chemical stability of the final material present important problems. Apparently, the wide scatter of the experimental results for the thermodynamic characteristics, critical parameters of superconductivity, *etc.* reported by different authors is due to this problem. Nevertheless, a number of important conclusions can be made.

1. Depending on the temperature of treatment of oxide HTSC materials by foreign molecules of simple compounds, the phenomena resulting from their effect on the superconductivity of these materials can be separated in two groups.

The phenomena observed on treatment of HTSC materials at temperatures up to 473 K correspond to the first group. As a rule, such treatment little affects superconductivity. It is important that this problem is far from clarified even now, despite numerous publications on this matter. The experimental results obtained by different groups of authors and the conclusions made on this basis on the nature of the effect are usually contradictory and inconsistent. Nevertheless, studies in this temperature range are very important for understanding the physicochemical processes that occur on superconductor surfaces.

The second group includes phenomena caused by treatment of HTSC materials at temperatures above 473 K. Such treatment often affects strongly the parameters of superconductors. As a rule, the experimental results obtained in different studies are reproduced satisfactorily. The effect of simple molecules on the properties of superconductors in this temperature range is caused by the intercalation of molecules in its crystal lattice and/or by their chemical reactions with the ions of an HTSC material. As a rule, the action of simple molecules at temperatures above 473 K results in superconductivity degradation.

Intercalation of oxygen, which plays a key role in the formation of the superconducting phase, deserves special attention. Numerous studies showed that halogen molecules or atoms incorporated in the lattices of HTSC ceramics can play the same role as the oxygen atoms. For example, the non-superconducting tetragonal phase of $YBa_2Cu_3O_{7-x}$ passes in the superconducting orthorhombic phase upon intercalation of halogens.

2. The range of effects of organic compounds on the characteristics of superconductivity is much more diverse. The first studies along this line carried out on low-temperature superconductors showed that the donor–acceptor interaction of organic molecules with the superconductor material results in a considerable change in the critical parameters of superconductivity. The changes in T_c and I_c correlate with the electronegativity of the adsorbed molecules. Similar phenomena were observed later in the studies of HTSC materials.

The superconductivity parameters of oxide materials depend on the electronic properties of adsorbed molecules or a deposited polymeric film. Dielectric polymers little affect superconductivity, whereas conducting polymers decrease T_c. This effect is apparently due to the 'proximity' effect.

It has been proven that intercalation of planar organic molecules into the space between the crystal lattice layers in HTSC materials changes their characteristics considerably. In some cases the specimens display unusual physical properties.

Adsorption of stable organic radicals affects the magnetic state of the superconductor surface and the electric resistance of the intergranular layers; as a result, I_c changes.

3. In turn, superconductivity can affect noticeably various physicochemical processes occurring on the superconductor surface. For example, transition of a material into the superconducting state changes the luminescence characteristics of organic dyes adsorbed on the surface of an HTSC material (the quantum yield and the position of the maximum in the luminescence spectrum). Systems in which the energy of interaction between the superconductor and paramagnetic molecules from the environment is comparable with the energy of the adsorption interaction were found among HTSC materials. Owing to this, superconducting membranes can separate gas mixtures of paramagnetic and diamagnetic molecules. At the liquid nitrogen temperature, the superconducting adsorbent adsorbs paramagnetic oxygen molecules several-fold more weakly than diamagnetic argon atoms. This is probably due to the repulsive interaction of the magnetic moment of the molecule with the magnetic flux 'uptaken' by the specimen granules.

4. The low-temperature heterogeneous-catalytic *ortho–para* hydrogen conversion occurring at the paramagnetic centres of the adsorbent is also very sensitive to the surface state, and its rate decreases by several orders of magnitude as the catalyst passes into the superconducting state. This phenomenon can be explained by shielding of the catalytically active paramagnetic centres located on the superconductor surface, which is caused by the substrate diamagnetism.

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