

CONFERENCES AND SYMPOSIA

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Scientific session '25 years of HTSC' of the Division of General Physics and Astronomy of the Russian Academy of Sciences and Joint Physical Society of the Russian Federation (19 December 2001)

A scientific session of the Division of General Physics and Astronomy of the Russian Academy of Sciences (RAS) and the Joint Physical Society of the Russian Federation dedicated to the 25th anniversary of the discovery of high-temperature superconductivity was held on 19 December 2001 in the conference hall of the P N Lebedev Physics Institute of RAS. The following reports were presented at the session.

(1) **Basov D N** (University of California, San Diego, USA) "IR spectroscopy of high-temperature superconductors";

(2) **Aksenov V L** (Joint Institute for Nuclear Research, Dubna, Moscow Region) "Neutron scattering by cuprate high-temperature superconductors";

(3) **Ponomarev Ya G** (Physics Department, M V Lomonosov Moscow State University, Moscow) "Tunneling and Andreev spectroscopies of high-temperature superconductors";

(4) **Kopaev Yu V** (P N Lebedev Physics Institute, RAS, Moscow) "High-temperature superconductivity models";

(5) **Gaponov S V** (Institute of Microstructure Physics, RAS, Nizhniĭ Novgorod) "Low-current devices and equipment";

(6) **Chernoplekov N A** (Russian Research Center 'Kurchatov Institute', Moscow) "State of the art in applied high-current superconductivity".

Abridged versions of four (2, 3, 4, and 6) reports are given below.

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Neutron scattering by cuprate high-temperature superconductors

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Cuprate high-temperature superconductors (HTSC) are extremely convenient objects for neutron scattering studies. The moderate complexity of the crystal structure with elements that differ considerably in atomic number and the presence of magnetic properties provide many possibilities for using neutron scattering in studies of the structure and dynamics of such compounds. The number of neutron scattering studies carried out from the time of the discovery of cuprate HTSCs is enormous, with the result that much useful information about the crystallographic and physical properties of such compounds was gathered. In Russia, the main research in neutron scattering involving high-temperature superconductors is done at the 'Kurchatov Institute' Russian Research Center, St. Petersburg Institute of Nuclear Physics of RAS, the Institute of Metal Physics of the Ural Division of RAS, and the Joint Institute for Nuclear Research (JINR).

Soon after the discovery of HTSC in neutron scattering experiments it was discovered that as the carrier concentration increases, the ordinary (commensurate) antiferromagnetic (AF) ordering of copper spins, which appears in the undoped state, rapidly deteriorates and that at a certain doping level x_c the Néel temperature vanishes. For doping levels higher than x_c instead of commensurate AF order there appear various forms of local (incommensurate) magnetism, which remain in the superconducting phase. Another amazing property of superconductors is, possibly, related to the remarkable magnetic properties of cuprate HTSC, and that is the emergence in the normal state in the underdoped region at a temperature T^* higher than the superconducting transition temperature T_c and the Néel temperature T_N of a pseudogap, a gap in the electron excitation spectrum.

The first indications of a pseudogap appeared in 1989. One of the first experiments in this area of research was done by physicists from JINR, who used neutron spectroscopy to study the crystal electric field (CF) [1]. The most interesting result that this method produced was related to studies of $HoBa_2Cu_4O_8$ and $Er_2Ba_4Cu_7O_{15}$ samples in the underdoped state with isotopic substitution of oxygen ^{18}O for ^{16}O [2]. The pseudogap opens at 170 K and 220 K for samples with ^{16}O and ^{18}O respectively. Thus, a large isotopic shift $\Delta T^* \approx 50$ K was observed. Estimates by analogy with the isotopic effect for T_c yield $\alpha^* = -2.2 \pm 0.6$. The experimental data imply that the characteristic time scale for the mechanism leading to the pseudogap isotopic effect is $10^{-8} \gg \tau > 10^{-13}$ s.

In recent years, thanks to experiments in neutron scattering on good, large single crystals with controlled values of x, researchers discovered a new phenomenon consisting in the emergence of incommensurate charge and spin ordering [3]. Understanding the evolution of spin dynamics under doping is a complex problem. The first experiments in 1989 and at the beginning of the 1990s showed the broadened AF Bragg peaks are constantly observed in samples with the highest values of T_c. Then it was found that the spin correlations are incommensurate.

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This manifests itself in the fact that the peaks in the scattering cross section in an insulator split into four peaks, and each of these peaks is shifted in Q by a small quantity δ. The present picture of the effect of doping on T_c is as follows. In the underdoped region, both δ and $T_c^{\max}(x)$ appear simultaneously and increase with doping in a similar manner. The saturation of T_c is expected to occur due to saturation of the number of carriers of the O(2p) type, while the decrease in T_c in the overdoped region is caused by the decrease in the dynamic coherence length of incommensurate spin fluctuations, which in turn may be caused by a decrease in the strength of the effective magnetic interaction as a result of the appearance of Cu(3d) type carriers. Anyhow it is clear that theories that promise to explain high-temperature superconductivity must explain the dynamic spin fluctuations.

Since the neutron has no charge, it does not interact directly with the static or dynamic charge structure in materials. However, the neutron can 'see' the charge structure through changes in atomic displacements. Over the years there have been many experiments that have studied phonons in HTSC. Various anomalies reflecting the features of structure and interaction in cuprates were discovered (e.g. see Ref. [4]). In recent years special experimental searches for the spatial modulation of the charge were carried out. Petrov et al. [5] studied high-energy longitudinal phonons in $YBa_2Cu_3O_x$ and found that the charge in superconducting cuprates, including the optimally doped case, is spatially inhomogeneous. Estimates of the domain sizes made on the basis of the data on the shape of the dispersionless part of the phonon branches yield 8×20 Å. An effective way to study the charge inhomogeneity in the CuO_2 plane may be to employ neutron spectroscopy of CF, since the CF potential at the site of the rare-earth ion situated between two neighboring CuO_2 planes is determined by the spatial distribution and the magnitude of the electric charge surrounding the rare-earth ion. Mirmelstein et al. [6] discovered charge ordering in $RBa_2Cu_3O_x$ ($R = Er, Ho$) in the form of bands $\approx a/2$ wide, which are severalfold smaller than the typical widths of stripes. At present the 'science' of stripes constitutes a broad area of research [3] that still contains many unresolved problems, the most important one being the role of stripes in superconductivity.

In recent years another effect observed in experiments on inelastic neutron scattering has been actively discussed. The effect was discovered in 1991 by J Rossat-Mignot and amounts to a resonance spin excitation (resonance peak) in the superconducting state and a gap in the spin excitation spectrum. The resonance peak has been present in many discussions: from the problem of the 'peak – dip – hump' structure to the superconducting pairing mechanism. However, a recent thorough analysis done by Kee, Kivelson, and Aeppli [7] has shown that although the resonance peak does accompany high-temperature superconductivity in cuprates, it cannot (due to its small spectral weight) provide a sizable contribution to observed phenomena.

Numerous studies have shown that the special features of the phase diagram are largely related to the strong antiferromagnetic exchange interaction, whose exclusive role has recently been corroborated in our experiments that studied the interrelationship between the superconducting transition temperature and the features of the structures in mercury-based HTSC [8 – 11]. The family of superconductors $HgBa_2Ca_{n-1}Cu_nO_{2n+2+x}$ was synthesized in 1993 by Antipov's group at the Chemical Department of M V Lomonosov Moscow State University by the crystallochemical modeling method. Among cuprates these compounds have the highest superconducting transition temperature. The group also established that it is possible, at least in principle, to attain transition temperatures $T_c = 150 - 160$ K under atmospheric pressure in structures in which the Cu – O distances have values realized in $HgBa_2Ca_{n-1}Cu_nO_{2n+2+x}$ structures under external pressure. In this connection, Hg-containing cuprates have been actively used in recent years as objects for studying the relationship between structure and superconducting properties. They are quite suitable for such studies since they possess optimal structures for manifesting superconductivity thanks to the absence of distortions caused by the incommensurability of the interatomic distances and the inhomogeneity of the cation distribution in adjacent layers. More than that, the structures of the first members of the homologous series contain only one type of oxidized element: the copper atoms in the CuO_2 layer. As a result, superconducting compounds of various compositions, from underdoped to highly overdoped, can easily be fabricated.

The compound that is structurally 'ideal' is Hg-1201 (a fragment of the structure of this compound is shown in Fig. 1). With Antipov's group we carried out systematic neutron diffraction studies of this compound both at normal and at various external pressures up to 5 GPa. The compressibilities of the lattice parameters and the basic interatomic distances are shown in Fig. 2 as functions of oxygen content [8, 9]. The compressibilities were defined as $\chi_y = -(1/y)\Delta y/\Delta P(10^{-3}\ \mathrm{GPa}^{-1})$ (y is the respective parameter). The samples were found to have the following values of T_c: 75 K for the underdoped sample, 97 K for the optimally doped sample, and 70 K for the overdoped sample. The x-dependence of T_c is well approximated by the formula $T_c = T_{c,\max}\left[1 - q(x - x_{opt})^2\right]$, where $T_{c,\max} = 97.8 \pm 0.8$ K, $q = 52 \pm 9$, $x_{opt} \approx 0.128 \pm 0.005$.

These data show that for low concentrations O_x the structure of the Hg-1201 compound is compressed isotropically, i.e. the compressibility of the principal interatomic distances corresponds to the compressibility of the unit cell. However, for high carrier concentrations the Hg – O2 and Ba – O1 bonds become almost incompressible, while the Cu – O2 and Ba – O3 bonds are compressed very strongly.

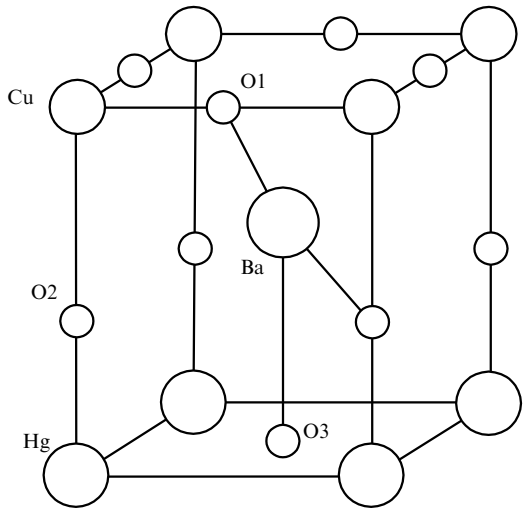

Figure 1. Fragment of the structure of the Hg-1201 compound.

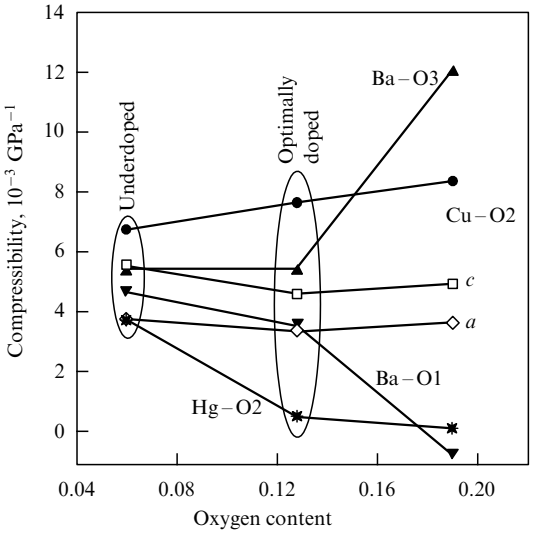

Figure 2. Compressibilities of the lattice parameters and the basic interatomic distances in the HTSC Hg-1201 as functions of oxygen content for three doping levels.

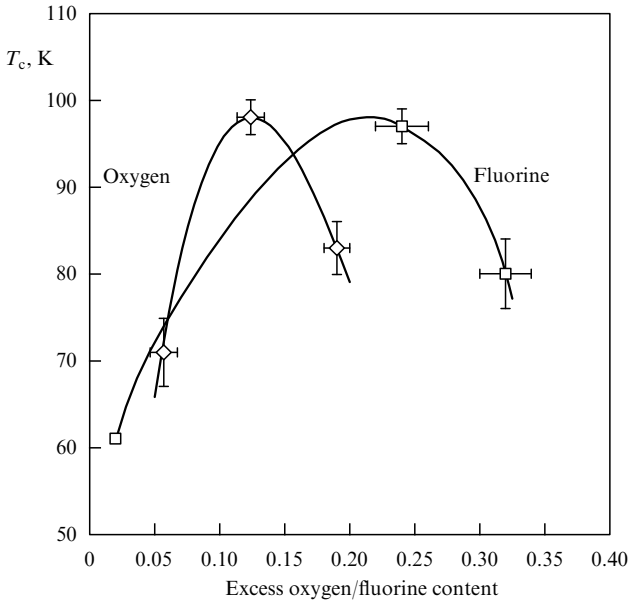

Figure 3. T_c plotted against the concentration of excess oxygen and fluorine in the Hg-1201 compound.

Thus, depending on the doping level, pressure leads to anisotropy of the structure and, in particular, to local changes in the CuO_2 layers responsible for superconductivity. In the overdoped state, the distance between these layers and the neighboring Ba cations does not decrease under pressure, while the apex anions (O2) are shifted considerably towards the copper cations. In the underdoped and overdoped structures, pressure leads to a decrease in the length of the Ba – O1 bond and a lower compressibility of the Cu – O2 bond. Such changes in the atomic separations and, as a result, in the atomic interactions caused by adding oxygen may be one of the reasons for the increase in charge transfer from the doping reservoir to the conducting CuO_2 layers in the overdoped state compared to underdoped and optimally doped superconductors. The fact that the compressibility of the structure is isotropic suggests that the effect of charge transfer from the doping reservoir to the CuO_2 layers does not play an important role in the structure of the Hg-1201 compound under pressure when $x \ll x_{opt}$. At the same time, the large shift of the Ba atoms under pressure in the overdoped state towards the HgO_x layers may be considered a manifestation of the increased charge transfer to CuO_2 layer, which leads to overdoping and a drop in T_c.

The increase in T_c under pressure is brought on by the increase in $T_{c,max}$ caused by an appropriate change in the interatomic distances. The role of replacement of additional oxygen with fluorine has been studied to research these effects. The thing is that fluorine has a lower formal valence than oxygen, which means that to achieve the same carrier concentration the amount of fluorine must be greater. More than that, fluorine has a smaller ionic radius. These factors can lead to a substantial change in bond lengths.

Figure 3 depicts the curves representing the dependence of T_c on the concentration of excess oxygen and fluorine in the Hg-1201 compound [10]. The anions of oxygen and fluorine exhibit similar crystallochemical behavior, despite the fact that their charges differ substantially (they are -2 and -1, respectively). Hence, within a simple model of charge transfer, for the same doping level the fluorine concentration should be twice that of additional oxygen. And this is indeed the case. However, structural studies done by high-resolution neutron diffraction analysis demonstrated that the amount of injected fluorine and oxygen is noticeably greater than it should be according to the optimal doping conditions at $V_{Ba} = V_{Hg} = +2$, $V_O = -2$, and $V_F = -1$. Actually, the experiments showed that $x_F = 0.24$ instead of $x_F^{opt} = 0.16$ and $x_O = 0.12$ instead of $x_O^{opt} = 0.08$. Hence, the doping mechanism in the Hg-1201 compounds amounts not only to oxidation of CuO_2 layers, as assumed earlier, but, possibly, also to oxidation of HgO_2 'dumbbells', while the formation of the conduction band is the result of the charge balance between these fragments of the structure.

Another important observation follows from the data on the dependence of T_c on the parameter a (twice the Cu – O1 bond length in the plane) (Fig. 4) [10]. The parabolic dependence with the maximum around $T_c = 97$ K at $a = 3.882$ Å is the same for both oxidized and fluorinated samples. This implies that the parameter a and the carrier concentration x_{Cu} are key parameters determining the value of T_c.

The change in the length of the apical Cu – O2 bond caused by anion exchange, when $x_F \approx 2x_O$, is substantial compared to the change in the bond length in the plane. An increase in the amount of the extra anions in the Hg-layer results in a compression of the Cu – O2 distance. These bond lengths are substantially different for the fluorinated and oxidized phases. They also differ from the Cu – O1 bond lengths in the plane. For instance, in phases with $T_c = 97$ K the difference reaches 0.04 Å, which is much larger than the standard deviations and the difference between the parameters c.

The reason for this remarkable phenomenon can be explained if we also allow for variations in the apical Hg – O2 bond length. In contrast to the previous case, this bond length is much larger in the fluorinated Hg-1201 sample than in the oxidized sample. These bond lengths change because of the shifts of the O2 atoms towards the more oxidized copper cations from 1.963 Å ($\delta = 0.057$) to

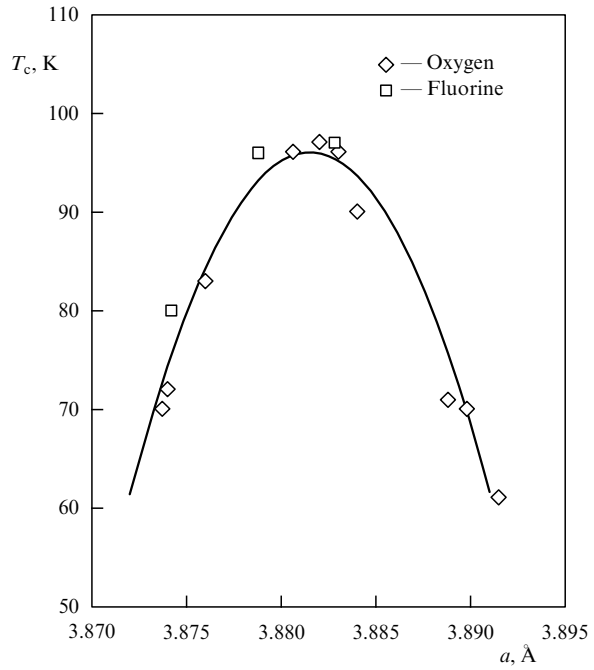

Figure 4. T_c plotted against the parameter a (twice the Cu – O1 bond length in the plane).

1.990 Å ($\delta = 0.19$) upon oxidation and from 1.990 Å ($\delta = 0.19$) to 2.01 Å ($\delta = 0.32$) upon fluorination.

As is known, the Hg – O2 bond is strongly covalent and even under high pressure its length does not reduce perceptibly: 1.980 (4) Å under normal pressure and 1.973 (19) Å under 5.07 GPa [8]. Hence the more plausible reason for the increase of the Hg – O2 bond length is the interaction of mercury with excess anions, even those which are located far from the Hg atom (rather than the change in the formal valence of copper). The increase in the coordination number of mercury caused by the injection of additional anions is accompanied by the shift of O2 atoms away from Hg cations towards Cu atoms in such a way that the Hg – O2 bond gets longer and the Cu – O2 bond, shorter. This implies that replacing the excess oxygen with a double amount of fluorine substantially changes the length of the apical Cu – O2 bonds, while the bonds in the plane and T_c remain unchanged. Formally such shifts may be interpreted as anisotropic compression of the CuO_6 octahedron along the c axis. Thus, from the above reasoning it follows that the compression of Cu – O1 bonds in the plane is the most plausible reason for the increase in T_c under pressure in mercury-based cuprate superconductors. This conclusion is also corroborated by the fact that upon fluorination of the Hg-1223 compound the parameter a decreases in comparison to its value in the oxidized sample: 3.8501 Å and 3.8524 Å, respectively [11]. The a-dependence of T_c for fluorinated and oxidized Hg-1223 samples differs somewhat from the similar dependence for Hg-1201 samples. In the case of the Hg-1223 compound, fluorination leads to compression of the structure in the ab plane, which leads to an increase in T_c. The a-dependence of the optimal T_c for the first three members of the series of mercury-based cuprate superconductors is an ideal straight line with the slope $dT_c/da \approx -1.35 \times 10^3$ K Å^{-1}. The compression of the parameter a reflects the decrease in the Cu – O bond length in the plane, since there is no bending of CuO_2 layers in the Hg-1201 compound and almost no bending in the Hg-1212 and Hg-1223 compounds. The reason for this linear behavior lies in the compression of the CuO_2 layer as the result of chemical modification of the crystal structure. The slope of the $T_c(a)$ curve is much larger than it is when external pressure is applied. From the value $dT_c/dP \approx 1.7 \times 10^3$ K GPa^{-1} and the crystallographic data we obtain the following estimate for the Hg-1223 compound: $dT_c/da \approx -1.6 \times 10^2$ K Å^{-1}. What is the reason for such a big difference? The thing is that, in contrast to external pressure, internal chemical pressure does not change the structural environment of a CuO_2 layer. These layers are flat in the Hg-1201 compound and almost flat in other compounds. The Cu – O – Cu angle in the plane is close to 180°: 178.4(4)° for Hg-1223 and 177.3(1)° for fluorinated Hg-1223.

On the other hand, external pressure changes the environment of CuO_2 layers, which is reflected in the greater compression of the apical Cu – O bonds and, as a result, in bending of these planes. For instance, the Cu – O – Cu angle in the plane becomes smaller than 175.0(5)° in Hg-1223 under $P = 2$ GPa, which ensures a similar rise in T_c but a much greater compression of bonds in the plane. The plane bending angle is an important parameter affecting superconductivity in layered cuprates. Compounds with higher T_c values have a smaller bending angle and larger apical distances for the CuO_5 pyramids.

Our structural studies (see Refs [8 – 11]) demonstrated the special role of AF exchange. Indeed, in mercury superconductors the CuO_2 plane has the smallest distortion: the bond angle Cu – O1 – Cu is close to 180°, which ensures the maximum strength of the AF exchange interaction. Under external pressure the length of the Cu – O1 bonds decreases, which leads to a further increase in the AF exchange. A typical value of $d \ln T_c/d \ln a$ in HTSCs is -4.5, while in 'phonon' superconductors this quantity has the opposite sign: $d \ln T_c/d \ln a = 12.5$ in MgB_2 and $d \ln T_c/d \ln a = 16$ in doped C_{60}. Internal chemical pressure upon fluorination leads to an even greater decrease in the Cu – O1 bond length and, hence, to an increase in the AF exchange and T_c: $d \ln T_c/d \ln a \approx -50$.

These features of the a-dependence of T_c and also the high values of T_c and the small isotopic effect in cuprate mercury-based HTSCs can be explained by the two-band Hubbard p – d model in the strong correlation limit, which amounts to the effective single-band t–J model [12]. The same model can explain the emergence of a pseudogap as the result of emergence of short-range dynamic magnetic clusters. Thus, all suggests that a pairing mechanism realized only in cuprates is driven by AF exchange and that the energy of this exchange reaches a record high value in view of the special features of the electronic structure of cuprates.

A separate topic in HTSC physics is the penetration of magnetic field into superconductors. By measuring the depolarization of a beam of polarized neutrons that has passed through the sample and using polarized neutron reflectometry it is possible to study the vortex structure in the bulk of the sample and to observe individual vortices [13, 14].

In conclusion I would like to note that the development of neutron scattering studies and support of research reactors in Russia has, to a large extent, been made possible through the State Program of High-T_c Superconductivity, later transformed into the Russian ANFKS state-sponsored R&D program, the Ministry of Science and Technology (currently

the Ministry of Industry, Science and Technology), and the Ministry of the Russian Federation on Atomic Energy.

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Tunneling and Andreev spectroscopies of high-temperature superconductors

Ya G Ponomarev

1. Introduction

Theoretical and experimental studies of the nature of high-temperature superconductivity are far from completion [1–4]. However, in the 15 years of studies of high-temperature superconductors (HTSC), studies that employed the most modern experimental methods, an enormous body of data has been gathered and theoretical models for describing the unique properties of HTSCs have been built. Note that even today there is no agreement in the choice of the pairing mechanism [5–8], although the existence of an isotopic effect in underdoped and overdoped cuprate superconductors is a clear indication of the important role that phonons play in the formation of the superconducting properties of HTSCs [5].

According to modern ideas [9–11], doped crystals of the cuprate superconducting compounds

$$Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4+\delta}\,, \qquad Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4+\delta}$$

and

$$HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$$

constitute a natural superlattice of the type SISI..., where S is a thin superconducting block containing one or more CuO_2 planes intercalated with calcium, and I is a layer of insulator (spacer) that, in particular, actuates doping of the CuO_2 blocks due to introduction of excess oxygen into the central part of the spacer. Since the dopant is outside the CuO_2 blocks, it has no significant effect on the hole relaxation time in the CuO_2 planes. Introduction of impurities (magnetic or nonmagnetic) into the CuO_2 planes rapidly suppresses superconductivity. In cuprate HTSCs the spacers occupy up to 80% of the crystal's volume, while only about 20% is occupied by the superconducting CuO_2 blocks. Spacers play an important role in forming the electron transport in the c-direction due to resonance tunneling [9, 12].

When the temperature is below T_c, a doped high-temperature superconducting crystal behaves as a stack of strongly coupled Josephson junctions, so that the superconducting current in the c-direction is of the Josephson nature (weak superconductivity). Note that the specific superconducting properties of layered crystals with Josephson coupling of layers were discussed in detail even before high-temperature superconductivity was discovered (Ref. [13], Chap. 6).

In pure cuprates, a CuO_2 plane with a half-filled 2D band proves to be unstable against a transition into the Mott insulator phase as a result of formation of long-range antiferromagnetic order (doubling the period causes the area of the 2D Brillouin zone to diminish by a factor of two). Light doping with oxygen destroys the long-range antiferromagnetic order, which leads to an insulator–metal transition and to the emergence of a hole Fermi surface of open type [14]. Here the Fermi level may be in the vicinity of an extended Van Hove singularity with giant peaks in the density of states in $\Gamma-M$ directions [5, 15].

High-temperature superconductivity occurs in CuO_2 planes within a relatively narrow interval of impurity hole concentrations p. The Fermi surface changes only slightly in the process [16]. According to photoemission spectroscopy data, the superconducting gap is largest in the $\Gamma-M$ direction (i.e. in the direction of a Van Hove singularity) and smallest in the $\Gamma-Y$ direction, in which the electron density of states passes through a minimum [17]. The gap anisotropy decreases substantially as p increases [18]. Note that at least in principle the Fermi level may get pinned to a Van Hove singularity within a certain interval of impurity hole concentrations p [19]. The superconducting transition temperature T_c varies with p according to a parabolic law (in the first approximation) [20].

2. Some experimental results obtained in HTSC studies using the tunneling and Andreev spectroscopy methods

When applied to HTSC, the methods of tunneling and Andreev (point-contact) spectroscopies demonstrated their efficiency and made it possible to extract useful information about the physical properties of these materials in the superconducting and normal states. Below I briefly discuss some recent experimental results of tunneling and point-contact measurements involving HTSC samples.

2.1 Intrinsic Josephson effect. Characteristic properties of the SISI... structure

An achievement that can be considered really important is the discovery and study in cuprate superconductors of the intrinsic Josephson effect [21–24], which clearly demonstrated the 2D nature of electron transport in HTSC. Thorough investigations of the intrinsic Josephson effect in various high-temperature superconducting materials actually led to the creation of a new method of studying layered superconductors, *the intrinsic tunneling spectroscopy method.*

Studies of the intrinsic Josephson effect in high-temperature superconducting mesastructures fully corroborated the SISI... model: (1) when $T < T_c$, multiple-branch current–