The energy gap in the electron excitation spectrum of oxide superconductors

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Analysis of results of investigations of the energy gap Δ in oxide high-T_c superconductors by the methods of the tunnel effect, electron photoemission, IR absorption, Raman scattering of light, and others, indicates satisfactory agreement of results obtained by different methods. For all the oxide superconductors with $T_c \gtrsim 30$ K the ratio $2\Delta/kT_c = 5$–6 is significantly greater than the value predicted by the BCS theory. The deviations of the experimental data near the edge and the bottom of the gap from the values that follow from the traditional model for the distribution in energy of the excitations are within the limits of accuracy of the measurements. The data obtained do not contradict the ideas concerning the electron-phonon mechanism of superconductivity in the oxide superconductors that have been investigated.

1. INTRODUCTION

Whereas the density of electron states $N_0(\varepsilon)$ in a normal metal near a Fermi surface is independent of energy, there is an energy gap Δ in the distribution of electron energies in the traditional superconductors.

The ideas that an energy gap possibly is what determines the superconducting properties of metals date from the mid-1930s, when F. London[1] formulated the hypothesis that the phenomenological equations that he suggested for the electrodynamics of superconductors could be understood from the microscopic point of view if one assumes the existence of such an interaction between the electrons that the excited energy states of the electrons will be separated from the ground state by a finite energy gap Δ_0. The difference of the energy gap in superconductors from the gap in semiconductors consists of the fact that, whereas the occurrence of a gap in semiconductors is determined by the periodic potential of the atoms of the crystal lattice, in superconductors the gap at the Fermi surface is formed as the result of interaction between the electrons and, as a consequence of this, the entire electron system, along with the gap, may be shifted with respect to the crystal lattice. Here, since the energy losses during motion can occur only in increments larger than 2Δ, there are no dissipative losses at low velocity. And this is actually a superconducting current, a current without losses.

Later on, it was determined that the interaction between electrons was determined by the exchange of virtual phonons. These ideas served as the starting point for the construction of the very successful Bardeen-Cooper-Schrieffer (BCS) theory.[2] This theory not only predicted an energy gap of the correct order of magnitude, but it was also able to explain most of the experimental data which existed at that time. The results of the BCS theory soon were obtained by other methods.[3,4] According to the BCS theory, the value of the energy gap Δ_0 at $T=0$ is universally connected with the critical superconductor temperature T_c by the relation

$$\frac{2\Delta_0}{kT_c} = 3{,}52. \tag{1}$$

For the isotropic case, the electron excitation energy E_K measured from the Fermi energy ε_F is

$$E_K = (\varepsilon_K^2 + \Delta^2)^{1/2}, \tag{2}$$

where ε_K is the unperturbed value of the energy. The density of the energy distribution of the excitations close to ε_F in a superconductor is

$$N_s(E) = N_0(\varepsilon)\frac{d\varepsilon}{dE} = N_0\frac{E}{(E^2-\Delta^2)^{1/2}} \tag{3}$$

(a possible $\Delta(\varepsilon)$ dependence is not taken into account). It is obvious that $|E|$ cannot take values smaller than Δ, and Relation (3) has meaning only for $|E|>\Delta$; for $|E|<\Delta$,

$$N_s(E) \equiv 0. \tag{3'}$$

As is evident from Relation (3), the density of the elementary excitation states of a superconductor $N_s(E)\to\infty$ as $|E|\to\Delta_0$. The Relations (1), (2), and (3) shown above have been verified by many experiments for traditional superconductors.

After the discovery[5] in 1986 of new oxide superconductors with $T_c > 30$ K, the problem of studying the $N_s(E)$ distribution and the value of Δ_0 arose for this class of materials. The solution of this problem was all the more necessary because the mechanism for the origin of superconductivity in these materials was not determined, and hypotheses were put forward that the superconductivity in them might have a qualitatively different nature.

Even in the course of the first attempts at the experimental determination of the value of Δ_0 in the excitation spectrum, it was determined that this problem has a number of peculiarities for this class of materials:

a) the oxide superconductors are complicated chemical compounds with relatively weak chemical bonding between the atoms; as a consequence of this, for most (if not for all) oxide superconductors, the surface layer undergoes such a strong change after a short time interval that its characteristics become qualitatively different from the properties of the original material. This circumstance is very significant for research on the energy gap by such methods as the tunneling effect, the electron photoemission method, and by optical methods in which the role of the surface is decisive.

b) A high value of the critical temperature (T_c up to 120 K) hinders the use of such traditional methods as the determination of Δ_0 from the temperature dependence of the heat capacity or thermal conductivity of the electrons since, in the temperature interval necessary for measurement ($T_c \approx 20$ K), the contribution from the lattice to these characteristics is great and possesses a complicated temperature

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dependence because of the presence of many modes of lattice vibrations.

c) At the same time, a large value for the energy gap enables one to use methods to determine it which were unsuitable for traditional superconductors because of limited equipment sensitivity (the electron photo-emission method).

The present paper contains an analysis of the experimental efforts that have been undertaken (up to November 1989) to determine by different methods the excitation distributions in high-temperature superconductors and to measure the values of Δ_0. We restricted ourselves to a review of the papers which determined the development of each of the procedures used, certainly without claiming to list all the papers written in this field, especially because many of them, especially at the first stage were as is now obvious, unsuccessful. Since the review sets itself the goal of examining experimental papers, the most impressive experimental curves are presented in it. The reader will not find in this paper a detailed review of a number of published experiments in which the researchers in general did not publish the gap peculiarities in the excitation spectrum since, after completion of the experimental procedures, their authors later on obtained completely satisfactory gap peculiarities, and the first publications are only of historical interest.

As will be evident from an analysis of the experimental research (see below), one discusses at the present time the following possible differences of $N_s(E)$ for the oxide high-temperature superconductors from the $N_s(E)$ for traditional low-temperature superconductors. First, such a sharp maximum of the density of states is not observed near the boundary of the gap for $|E| \to \Delta$ as follows from Relation (3), and second, a finite density of states is observed for $|E| \ll \Delta_0$. Special attention is paid in the review to these two peculiarities of the results of investigating the properties of oxide superconductors.

The paper is divided according to the methods which the authors used to determine the energy gap. A summary of the most reliable, in the author's opinion, values of Δ_0 that have been obtained in different experimental papers, is presented at the end.

2. THE TUNNELING EFFECT

In the case of traditional superconductors, the most complete information about the density of states near the Fermi surface and the value of the energy gap was obtained by means of the tunneling effect procedure. The technique of such experiments was first described by Giaever,[6] who also used it to investigate superconductors.

The tunneling current between two metals separated by a dielectric layer, whose transmittance for electrons w is independent of the direction of the current, is determined by the relation

$$I(V) = \int_{-\infty}^{+\infty} w(E)\, N_1(E - eV)\, N_2(E)\, (f(E - eV) - f(E))\, \mathrm{d}E, \tag{4}$$

where V is the potential difference between the metals, N_1 and N_2 are the densities of the electron states in the metals, and $f(E)$ is the distribution of the Fermi electrons over different states. Assuming that $w(E) \equiv w_0$ and $kT < \varepsilon_F$, for normal metals, we find

$$I_{nn}(V) \equiv w_0 N_{1n}(\varepsilon_F)\, N_{2n}(\varepsilon_F)\, V = G_{nn} V, \tag{5}$$

i.e., the current through the barrier is determined by the conductance G_{nn} independently of voltage and temperature. Relation (5) is valid only in the range of low voltages for the case of symmetric barriers. In the case that one of the metals is a superconductor (a s–n junction),

$$I_{ns}(V) = G_{nn} \int_{-\infty}^{+\infty} \frac{N_{1s'}(E)}{N_{1n}(\varepsilon_F)} (f(E - eV) - f(E))\, \mathrm{d}E, \tag{6}$$

and considering that, for $T = 0$,

$$\begin{aligned} f(E) - f(E + eV) &= 1 \quad \text{for} \quad 0 < E < eV, \\ &= 0 \quad \text{for} \quad E < 0,\ E > eV, \end{aligned} \tag{7}$$

$$I_{ns} = G_{nn} \int_0^V \frac{N_{1s}(E)}{N_{1n}(\varepsilon_F)} \mathrm{d}E,$$

and for differential conductance, we find

$$\frac{\mathrm{d}I_{ns}}{\mathrm{d}V}(V) = \frac{G_{nn}}{N_{1n}(\varepsilon_F)} = N_{1s}(eV). \tag{8}$$

Thus, by measuring the differential conductance at a temperature close to absolute zero, one may determine the density of states for a superconductor.

After using Expression (3) for the density of states, we shall find that, for $T \to 0$

$$\begin{aligned} I_{ns} &= 0 \qquad\qquad \text{for} \quad eV < \Delta_0, \\ &= (eV^2 - \Delta^2)^{1/2} \quad \text{for} \quad eV > \Delta_0. \end{aligned} \tag{9}$$

In the case of finite temperatures $T \neq 0$

$$I_{ns} = 2G_{nn} \frac{\Delta}{e} \sum_{m=0}^{\infty} (-1)^{m+1} K_1\left(\frac{m\Delta}{kT}\right) \operatorname{sh} \frac{meV}{kT}, \tag{10}$$

where K_1 is a modified first order Bessel function of the second kind. For $V \to 0$, this expression reduces for $T \approx 0$ to

$$I_{ns}\big|_{\substack{V\to 0,\\ T\to 0}} = I_{nn} \left(\frac{2\pi}{kT}\right)^{1/2} \exp\left(-\frac{\Delta}{kT}\right), \tag{11}$$

i.e., it enables one to determine Δ_0 by yet another method.

In the case that both metals in contact are superconductors, for simplicity and for the same purpose $\Delta_1 = \Delta_2 = \Delta$, for $T \to 0$

$$\begin{aligned} I_{ss} &= 0 \quad \text{for} \quad V < \frac{2\Delta}{e}, \\ &= G_{nn}(2\Delta + eV)\, E(\alpha) - 4\frac{\Delta(\Delta + eV)}{2\Delta + eV} K(\alpha) \quad \text{for}\ V > \frac{2\Delta}{e}, \end{aligned} \tag{12}$$

where

$$\alpha = \frac{eV - 2\Delta}{eV + 2\Delta},$$

and $K(\alpha)$ and $E(\alpha)$ are complete elliptic integrals. Since

$$\lim_{\alpha\to 0} K(\alpha) = \lim_{\alpha\to 0} E(\alpha) = \frac{\pi}{2},$$

then, for $eV \to 2\Delta$, the current that is given by Expression (12) undergoes a discontinuity, and specifically

$$I_{ss}\big|_{\substack{T\to 0,\\ eV\to 2\Delta}} = G_{nn} \frac{\pi}{2} \frac{\Delta}{e} = I_{nn} \frac{\pi}{4}. \tag{13}$$

This discontinuity in the magnitude of the current is also

preserved at finite temperatures right up to T_c, which enables one to determine the $\Delta(T)$ relation most reliably.

In the case of traditional superconductors, the experimental results agree completely satisfactorily with the conclusions of a theoretical investigation of the tunneling process, although for a number of superconductors, for example, V, Nb_3Sn, and Nb_3Ge, satisfactory agreement was achieved only after many unsuccessful attempts. In the first stage of the research, until the time when the procedure for preparing a tunneling junction on a clean superconductor surface was mastered, the gap peculiarities on the experimental curves were hardly distinguishable.

2.1. An investigation of the compounds $La_{2-x}Si_xCuO_y$ and $YBa_2Cu_3O_y$

2.1.1. A normal metal-superconductor junction. In the first attempts to determine the tunneling characteristics of oxide superconductors, a sharp tip of some metal (Nb, W, Pt, Ir, etc.) was pressed to their surfaces. One attempted to connect the non-linearities in the I(V) characteristics found here with the value of Δ_0. Usually the state of the surface and junctions in these experiments was uncontrollable.

Moving the tip relative to the surface of the specimen was accomplished by means of both a mechanical and also a piezoelectric system. The distance between the tip and the surface of the specimen was usually monitored by the magnitude of the tunneling current.

In the most complete systems of the scanning tunneling microscope type, three degrees of freedom for moving the needle enable one (at least in principle) to investigate the topography of the contact characteristics of the surface of the test object. It is especially important in this method that the junction be made between very clean surfaces; otherwise, the insignificantly small current through the junction are (of the order of the size of an atom) will not be resolvable at the level of sensitivity of the instrument (apparatus).

Ceramic specimens were the first test objects. The compound $La_{2-x}Sr_xCuO_{4-\delta}$, $x = 0.1$ to 0.2, $T_c \approx 36$ K was the first to be investigated in 1987 by this method.[7,8,9] The tunneling characteristics obtained[8,9] were still far from perfect, but nevertheless they enabled one to estimate the value of Δ_0 and from it to calculate the ratio $2\Delta_0/kT_c$, which turned out to be equal to 5.8 ± 2 and 4, respectively.

The quality of the tunneling characteristics improved after the surface of a specimen obtained by cleaving at liquid helium temperatures[10] became the test object, although even in this case, the gap peculiarities were not very clearly pronounced. The authors quite naturally (a polycrystal was the test object) connected this with the hypothesis that, in reality, some distribution of the value of Δ_0 near the most probable value occurs. The tunneling characteristics calculated by this hypothesis that are compared with the experimental data (Fig. 1) were found to be in qualitative agreement and enabled one to estimate the value of Δ_0. We note that in these experiments the value of dI/dV in a region of low potential V applied to a tunneling junction amounts to less than 5% of the value of dI/dV for $eV > \Delta$. It is clear that the value

$$\beta = \frac{dI}{dV}\bigg|_{V\to 0} \left(\frac{dI}{dV}\right)^{-1}\bigg|_{eV>\Delta}$$

enables one to estimate the fraction of normal excitations for $|E| \ll \Delta$ near the bottom of the gap. An obvious correlation

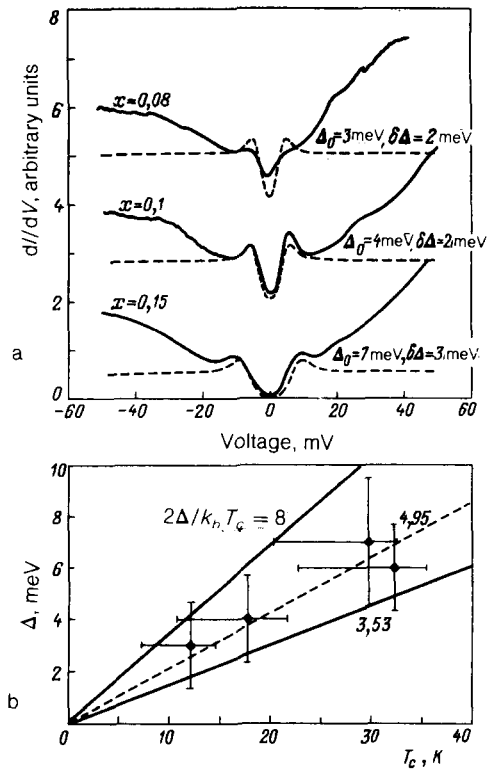

FIG. 1. a) Tunneling characteristics of $La_{2-x}Sr_xCuO_4$: the BCS theory, assuming that Δ has a Gaussian distribution around Δ_0. The zero points of the curves for $x = 0.1$ and 0.08 are shifted vertically by 2 and 4 units, respectively.[10] b) Δ_0 and T_c of the specimens investigated.[10]

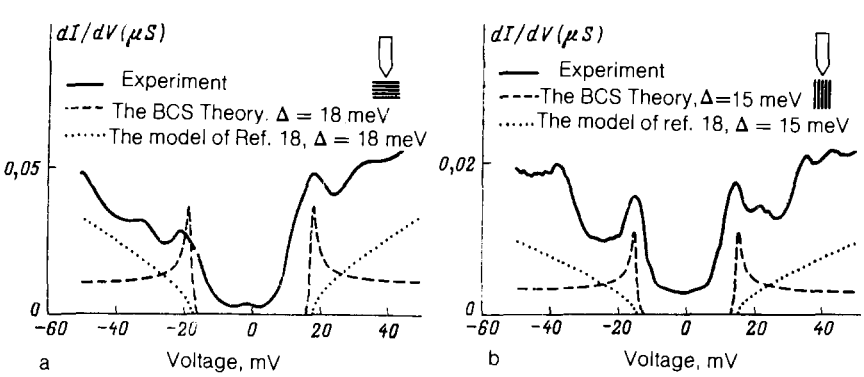

FIG. 2. a) Tunneling characteristics of a YBaCu crystal along different axes.[17] b) Comparison of the experimental curves with the standard BCS theory and model[18] which considers the tunneling of many particles.

between the value of Δ_0 and T_c of the specimen being investigated was noticed in this paper (Fig. 2a). $2\Delta_0/kT_c = 4.95$ averaged over all the specimens investigated.

Ceramic specimens also served as the first objects in investigating the tunneling effect in the compound $YBa_2Cu_3O_{7-\delta}$ with $T_c \approx 90$ K.[11-16] Already the first papers showed that the state of the surface plays a decisive role in the results of an investigation. For example, the gap peculiarities were generally not detected on the polished surface of a specimen.[11] The form of the characteristics varied with the load applied to the junction; in reality, it might be caused by tunneling between individual superconducting ceramic granules, etc. All this indicated the need for definite skepticism in analyzing the experimental curves and determining the value of Δ_0 from them.

One could have intended to obtain unambiguous results by using single crystal specimens. As an example, let us turn to Ref. 17, in which the authors achieved a junction parallel and perpendicular to the CuO planes (the plane a,b) in a YBaCuO crystal, as is illustrated in Fig. 2. The characteristics obtained are compared with calculations according to a model with a distribution of the gap around an average value, and with a model of tunneling between many superconducting granules that has been examined in Ref. 18. The authors quote $4.5 < 2\Delta_0/kT_c < 6$ and $3.9 < 2\Delta_0/kT_c < 4.2$ for the *a* and *b* cases, respectively. This paper is interesting as the first attempt to determine the anisotropy of the gap in this compound, although the results obtained in it are unconvincing, considering the form of the tunneling peculiarities.

Later on, this same group of authors,[19] in describing the scanning tunneling microscope procedure, quotes a number of completely acceptable tunneling characteristics for a number of materials (Fig. 3). To achieve a tunneling transition in the experiments, it was necessary to break down mechanically the non-conducting layer which covers the surface of the super-conductor with the needle of the scanning tunneling microscope. Of course, this operation could lead to significant distortion of the characteristics of the specimen under investigation, for example, as a consequence of

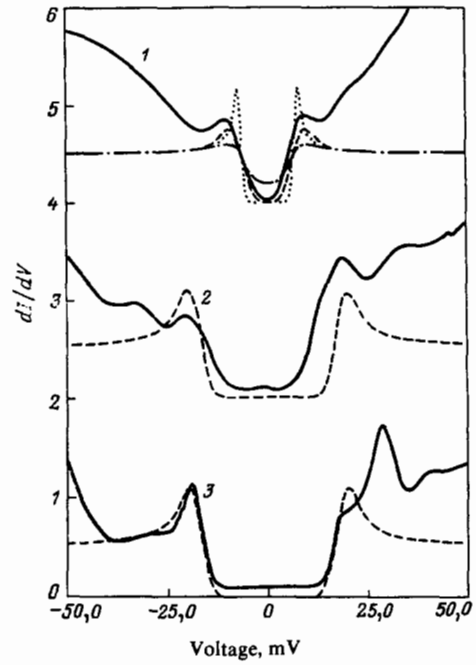

FIG. 3. Tunneling characteristics $(dI/dV)(V)$ for a contact of a PtRh needle with 1) $La_{1.85}Sr_{0.15}-CuO_4$; 2) a $YBa_2Cu_3O_7$ crystal, and 3) a $YBa_2Cu_3O_7$ film.[19] The solid curves are experimental curves raised by 4, 2, and 0 units, respectively. The symbols in Fig. 1 are the BCS theory with $\Delta = 7$ meV. The dash-dotted curve is for calculation according to a model which allows for quasiparticle damping, and the dashed curve is for calculation according to a model with a Gaussian distribution of the gap.

the presence of additional current not of tunneling origin flowing through the surface layer, or of a change of the characteristics of the superconductor under the needle because of its pressure.[20,21,22]

An ingenious procedure,[23] in which the needle of the scanning tunneling microscope is first used to break down the surface layer, and then the tunneling characteristics are determined at the same place by means of a subsequent bringing down of the needle (Fig. 4) is a development of the scanning tunneling microscope procedure in its use for in-

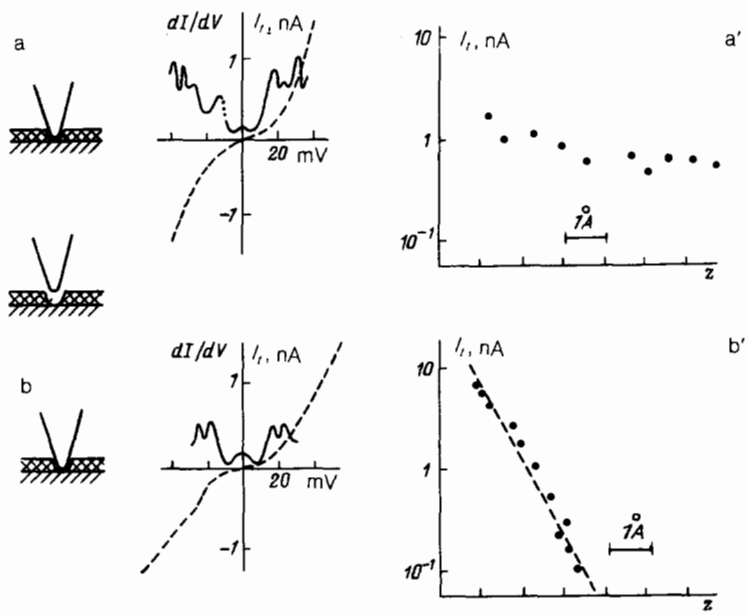

FIG. 4. A method for obtaining tunneling characteristics for a Scanning Tunneling Microscope.[23] a) The contact has penetrated into the surface layer; the dashed curve is $I(V)$ and the solid curve is the $(dI/dV)(V)$ relation. a') is the relation of the current to the needle displacement; the lack of an exponential relation is evident. b) A repeated bringing down of the contact; in the center are the characteristics $I(V)$ and $(dI/dV)(V)$. b') The current through the contact as a function of the displacement z of the needle; and exponential dependence of the current on z is evident.

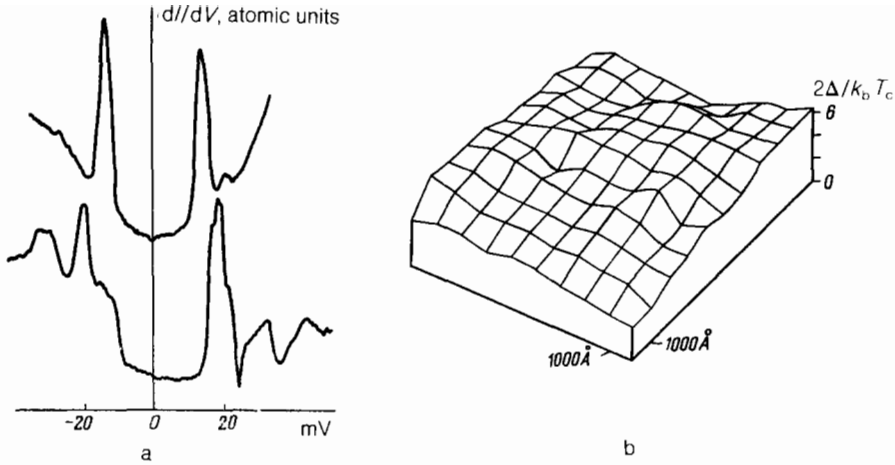

FIG. 5. a) The dI/dV characteristics of two contacts have been made over a 1,000 Å distance on the surface of a single crystal.[23] b) The topography of the change of $2\Delta_0/kT_c$ along the surface of a single crystal of $YBa_2Cu_3O_{7-\delta}$.[23]

vestigating oxide superconductors. The main advantage of this method consists of the fact that it enables one to use the scanning tunneling microscope as it is designed to be used, i.e., to measure the change of Δ_0 along the surface of the specimen.

The experiment showed[23–25] that a significant change of Δ_0 occurs along the surface in the microcrystals presented by the authors (Fig. 5), especially in the case of investigating the $YBa_2Cu_3O_{6.32}$ specimen (see Figs. 5 and 6).

The fact is significant that, whereas the change of the value of Δ_0 along the surface of a microcrystal reaches a factor of 1.5 for an area of $(\sim 1/\mu m)^2$, for individual measurements when, according to the estimates of the authors, the area of the junction amounts to $(2\ nm)^2$, clear tunneling peculiarities no different from those which are usually evident for traditional superconductors at $eV \approx \Delta$ may be obtained.

By averaging the value of Δ_0 along the surface,[24] the authors established a proportionality between the averaged value of $\overline{\Delta}_0$ and the value of T_c which was determined from electrical measurements. The ratio found by this method is $2\overline{\Delta}_0/kT_c = 4.4 \pm 0.1$. This operation is not completely well founded, since the change of the resistance of a specimen is determined by the presence of superconducting filaments, the probability of the occurrence of which at a given temperature is not directly connected with the averaged value $\overline{\Delta}_0$.

The question of whether the change of Δ_0 along the crystal surface is inherent to the YBaCuO system or is caused by defects in the procedure of preparing the crystals which were available to the researchers remains open in this series of papers.

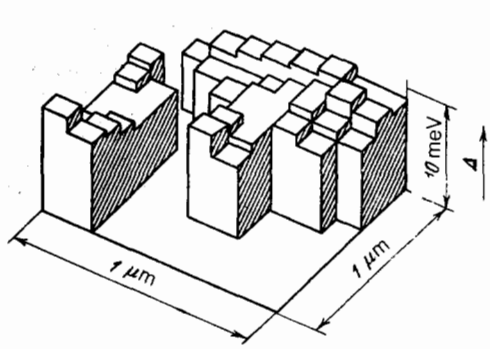

FIG. 6. The distribution of the energy gap along the surface of a single crystal of $YBa_2Cu_3O_{6.32}$.[25]

We note that a displacement in time of the locations of gap peculiarities with retention of the general form of the (dI/dV) (V) relation was noticed during scanning tunneling microscope measurements in several papers.[26,27] The nature of this effect has not been studied.

The scanning tunneling microscope is an irreplaceable instrument for investigating the perfection of specimens, although its possibilities in connection with oxide superconductors are significantly limited by both the presence of a modified surface layer and also by the impossibility or determining the variation of the tunneling characteristics with temperature during a rise of the temperature of the specimen to T_c, which is necessary in order to determine the $\Delta(T)$ dependence and to connect the value of Δ_0 with the true value of T_c at the site of the junction. To a significant degree these very circumstances compel one to treat with caution the $2\Delta_0/kT_c$ values determined from the tunneling characteristics that have been obtained by means of scanning tunneling microscopes.

Efforts have been undertaken recently to create procedures for preparing stable tunneling junctions similar to the tunneling junctions for traditional superconductors. Both freshly prepared films of oxide superconductors prepared according to a special procedure without additional oxidation, and also chemically cleaned specimen surfaces are used for this. A counterelectrode film is applied onto all these objects immediately after their preparation. The first encouraging results have been obtained in these efforts.[29–32] For example, in Ref. 32 tunneling junctions were prepared using a YBaCuO crystal, the form of whose characteristics was easily reproducible and independent of the counterelectrode material. However, as is evident from Fig. 7, the form of the dI/dV curves is only remotely reminiscent of the gap curves: the peculiarity at $eV = \Delta$ is indistinct, and the value of dT/dV is relatively large at $V \to 0$. One found similar characteristics in the case of traditional superconductors in the initial stage of tunneling research on such superconductors as V, Nb_3Sn, etc., and, as was found out later on, they reflected drawbacks of the procedure which was used to prepare the tunneling junctions. Evidently a similar situation also occurs at present for tunneling junctions in oxide superconductors prepared by the methods enumerated above.

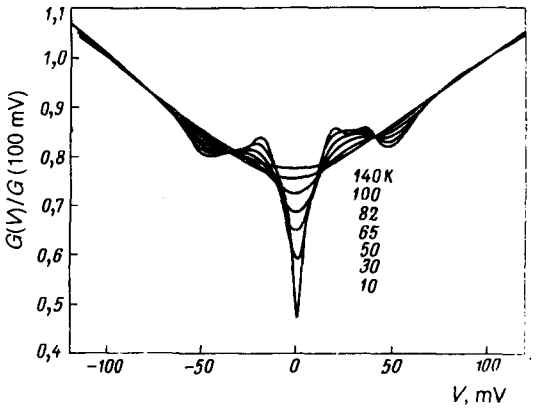

FIG. 7. The temperature dependence of the relative conductance $G = (dI/dV)(V)/G(100\ \text{mV})$ for a $YBa_2Cu_3O_7$ single crystal junction. The counterelectrode is lead in a normal state. The presence of $\Delta_1 = 19$ meV and $\Delta_2 = 4$ meV is assumed.[32]

We note that a "fresh" material surface obtained by means of fracturing the specimen was also used earlier in preparing tunneling junctions. Of these papers, we note Ref. 33, in which the anisotropy of Δ_0 in the compound YBaCuO was determined (Fig. 8). The superconductor film was epitaxially deposited onto a $SrTiO_3$ substrate, so that the required crystallographic axis was directed along the surface of the substrate. Next, as is shown on the insert in Fig. 9, a chip of substrate with film was made. An end of the film was brought into contact with lead. By comparing the values of T_c and values of Δ_0 measured in the directions parallel and perpendicular to the planes *a,b*, the authors of Ref. 33 obtained values of $2\Delta_0/kT_c$ equal to 5.9 ± 0.2 and 3.6 ± 0.2, respectively for these directions. The anisotropy of Δ_0 obtained in Ref. 33 is significantly greater than the data of Ref. 17, which evidently reflects a more successful procedure for preparing test objects.

Before going to the results obtained in investigations of other oxide superconductors, let us turn to experiments in which a superconductor-superconductor tunneling junction was investigated. Let us restrict ourselves to consideration of the papers in which a junction of identical oxide superconductors was investigated.

2.1.2. A superconductor-superconductor junction. It is well

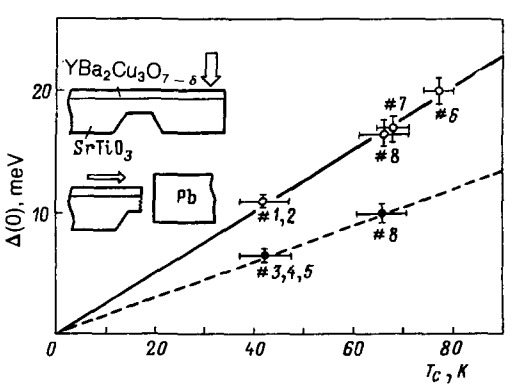

FIG. 8. Measurement of the gap anisotropy by using an epitaxial YBaCu film: the relation between Δ_0 and T_c for different specimens; the circles and dots are for a contact along and perpendicular to the CuO layers, respectively.[33] In the insert is the layout of the method for producing a contact.

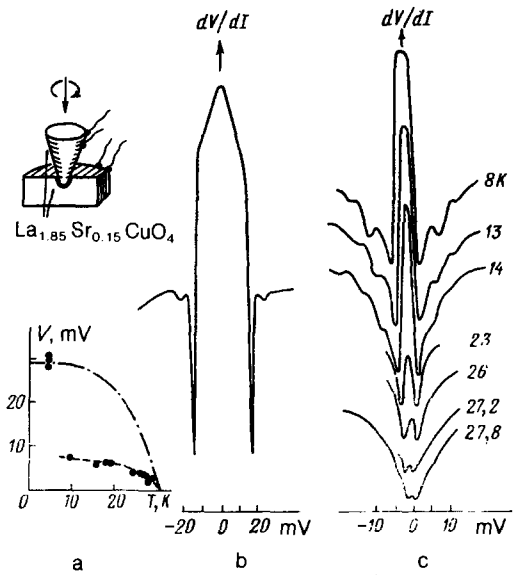

FIG. 9. $(dV/dI)(V)$ for a $La_{1.85}Sr_{0.15}CuO_4$-$La_{1.85}Sr_{0.15}CuO_4$ contact. a) Procedure for producing a contact. b) the characteristics of a contact with Δ_{max} ($T = 4.2$ K). c) Temperature dependence of the characteristics with Δ_{min}. At the bottom of Fig. 8a is the variation of 4Δ (the distance between dips) with temperature for Δ_{max} and Δ_{min}.[34]

known that the peculiarities at $eV = 2\Delta$ in superconductor-superconductor tunneling junctions may be investigated up to T_c of the material being investigated.

One of the first attempts to determine the value of the gap for a s–s junction was undertaken in Ref. 34. The authors used ceramic specimens of $La_{3-x}Sr_xCuO_y$ and $YBa_3Cu_3O_{7-\delta}$, which were brought into mechanical contact with a needle of the same material.

A mechanical device enabled one to carry out both translational and rotational motions of the needle (see the insert in Fig. 9). The experiments showed that one could obtain satisfactory characteristics only after breaking down the surface layer and penetration of the needle into the interior of the specimen. In a number of cases, one succeeded in obtaining for a lanthanum system junction characteristics with a very sharp peculiarity at $eV = \Delta_0$ which approach the ideal characteristics (Fig. 9). The difference from the ideal consisted of the finite increase of the value of $(dV/dI)(V)$ at $V \to 0$, which could be associated with the presence of a current of non-tunneling origin through the junction. The sharp dips for the $(dV/dI)(V)$ relation were connected with the appearance of peculiarities at $eV = 2\Delta_0$, and the distances between them are connected with the value 4Δ.

One did not succeed in using such a junction to determine $\Delta(T)$. A sharp change of the characteristics of the junction towards the form represented on the right of Fig. 9 occurred during heating of it in all the attempts. A junction with such characteristics was stable and allowed thermal cycling from 4.2 K to $T_c = 32$ to 33 K (based on the disappearance of the tunneling peculiarity). The thermal origin of the characteristics of this junction is represented on the right, which shows how the dips on the $(dV/dI)(V)$ curves gradually, draw closer and the maximum at $V = 0$ decreases with increasing temperature. The temperature dependence of the distance between the dips, which corresponds to the value 4Δ, is represented on the left in Fig. 9. Also the upper curve here shows the results of several experiments with the

characteristics shown on the left. This type of characteristics turned out to be more stable for a s–n junction, the results of experiments with which are denoted by small circles (rescaled by a factor of 4Δ). Using the value $T_c = 32$ K from tunneling measurements, we find that the maximum and minimum values of the gap in the $La_{1.85}Sr_{0.15}CuO_4$ compound that is investigated are $2\Delta_0/kT_c = 5.2 \pm 0.2$ and 1.35 ± 0.05, respectively.

In the case of a YBaCuO-ceramic junction with $T_c \approx 60$ K, the junction characteristics obtained were not so sharp and corresponded to $(2\Delta_0/kT_c)_{max} = 7.5$ and $(2\Delta_0/kT_c)_{min} = 1.7$.

Of course, since ceramic specimens were used in the experiments, there is arbitrariness in the treatment of the results obtained, mainly in the explanation for the abrupt change of the characteristics. One of the possible explanations of this fact is the hypothesis that, as a consequence of the layered structures of the materials under investigation, an end-to end junction of the layers is mechanically less stable in comparison with a plane-plane junction. If one accepts this hypothesis and assumes the presence of an anisotropy Δ_0, then the most unstable value Δ_{max} probably corresponds to an end-to-end junction of the CuO layers.

The main results of these experiments are that, in them, it was shown that

a) there is a possibility of obtaining tunneling characteristics which approach ideal ones for oxide superconductors, and

b) the value of $2\Delta_0/kT_c$ for oxide superconductors can significantly exceed the value $2\Delta_0/kT_c = 3.52$ from the BCS theory.

A similar procedure for creating a s–s junction was also used in Ref. 35 to investigate $Mba_2Cu_3O_7$ systems, where M can be Y, La, or Lu. The authors succeeded in obtaining characteristics with clear peculiarities at $eV = \Delta$ and at $eV = 2\Delta$. The value of Δ determined from these results for all the systems investigated lies within the limits $4 < 2\Delta_0/k\,T_c < 6$.

Another method for creating a s–s junction consists of fracturing a specimen at liquid helium temperatures.[36] In these experiments the inner surface of the specimen is first "bared" by means of the break, and then, after a certain time that is needed for the formation of a surface film, the boundaries of the break are joined again. One of the most convincing characteristics obtained by such a method for $YBa_2Cu_3O_7$ is shown in Fig. 10. Using it for calculation leads to the value $2\Delta_0/kT_c = 4.8$.

The dependence of the characteristics obtained on the conditions of the junction is the main drawback of the papers considered in this section. The form of the characteristics changes with the type of junction; from a normal metal (or superconductor)-semiconductor with a broad maximum of resistance at $V \to 0$ to a superconductor-superconductor junction with a resistance which approaches zero at $V \to 0$. A large number of additional peculiarities that are possibly connected, for example, with breaking down by the measurement current of individual superconducting microjunctions or with inhomogeneity of the junctions, may be present for the characteristics. Of course, these remarks apply to all junction measurements. Therefore, attempts to ascribe the peculiarities of the volt-ampere characteristics at $eV > \Delta$ to manifestations of the phonon spectrum are hardly well-founded, the more so because the locations of these peculiarities on the different experimental curves do not agree (for example, compare the two curves in Fig. 5). Considering this, we shall not discuss these peculiarities. Let us notice that an asymmetry of the tunneling $I(V)$ curves is usually noticeable for s–n junctions. This asymmetry is connected in Ref. 37 with the characteristics of the tunneling effect in the case of the superconductance of holes.

2.2. Tunneling research for other oxide superconductors

The metal oxide superconductors $BaPb_{0.75}Bi_{0.25}O_3$ with $T_c \approx 11$ K and $Ba_{1-x}K_xBiO_3$ $(0.4 < x < 0.6)$ with T_c right up to 30 K contain no copper at all. Whereas, according to Ref. 38, $2\Delta_0/kT_c \approx 3.2$ for the first compound, according to the first report[39] $Ba_{1-x}K_xBiO_3$ turned out to be a gapless superconductor, but according to a second, more

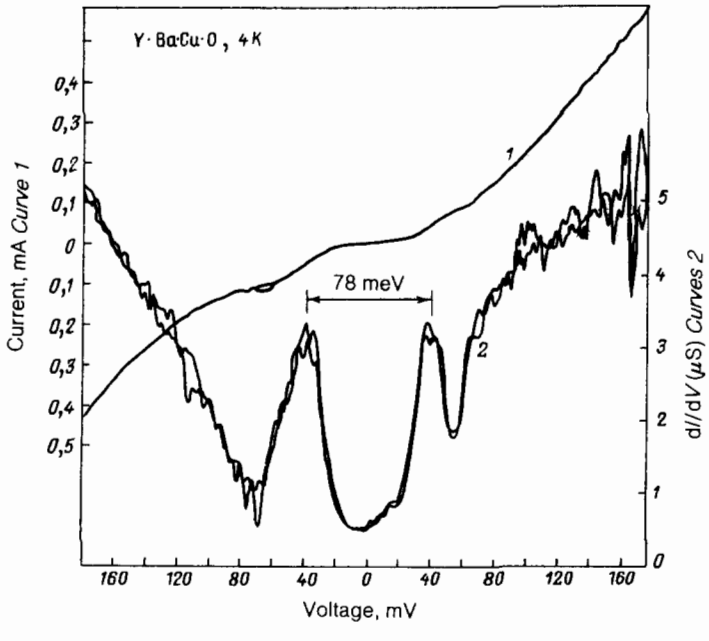

FIG. 10. The $I(V)$ and (dI/dV) (V) characteristics for a YBaCuO s-contact at 4.2 K that has been obtained by the fracture method.[36]

precise report, it has a gap with $2\Delta_0/kT_c \approx 3.9$ to 4.4. This is one of those papers in which, as the same authors extend and intensify their research, they make the original results more precise.

Let us now turn to research on the $Bi_2Sr_2CaCu_2O_y$ system with $T_c \approx 90$ K. An attempt was undertaken in crystals of this compound also to determine the crystallographic anisotropy of Δ by using surfaces that have been obtained by cleaving the crystal along and perpendicular to the CuO layers. It was observed that $2\Delta_0/kT_c = 4.9$ to 5.3 and 4.2 to 5 perpendicular to and along the layers, respectively. The authors assume that the results obtained along the layers are unreliable, since cleavage perpendicular to the CuO which was used in these measurements, was reminiscent of a small ream of sheets under a microscope. Let us recall that crystals of this compound are easily separated along the CuO planes. It is possible that the distorted form of the tunneling characteristics obtained for this cleavage is connected with this circumstance. $2\Delta_0/kT_c = 3.4 \pm 4.2$ was obtained in this same paper for a bismuth ceramic with $T_c = 110$ K.

It was shown earlier[41] in the course of investigating a polycrystalline specimen of $Bi_4Ca_3Sr_2Cu_4O_{16.3}$ with $T_c \approx 80$ K by means of a scanning tunneling microscope with a PtIr needle[43] that Δ_0 varies along the surface even for distances up to 1,000 Å, and that $2\Delta_0/kT_c = 4.5$ to 6.5. $2\Delta_0/kT_c = 8.7$ was obtained[42] for a specimen with composition $Bi_2(Sr_{0.6}Ca_{0.4})_3Cu_2$ and $T_c \approx 80$ K. The fact that a film of SiO_2 of 160 Å thickness was used as an insulator was the distinguishing feature of this paper. In the case of traditional superconductors, this procedure enabled one to master the procedure for creating tunneling junctions for complicated superconducting compounds, such as Nb_3Sn, Nb_3Ge, etc. The authors[42] used as indium film as a counterelectrode. The authors could investigate the origin of the $(dT/dV)(V)$ characteristics from 4.2 K to 200 K, which differs significantly from the predictions of the BCS theory, and which, in the opinion of the authors, requires additional analysis.

As was already pointed out, BiSrCaCu crystals cleave readily along the CuO planes, which enables one to obtain a clean surface of this material. An attempt was undertaken in Ref. 43 to prepare a tunneling junction on this surface, that has been obtained by cleaving, by spraying on lead or niobium as a counterelectrode. The best results were obtained with niobium. Peculiarities that are remotely reminiscent of gap peculiarities are evident for the characteristics; these disappear at $T > T_c \approx 85$ K. The $\Delta(T)$ relation obtained agrees with the BCS theory. The ratio $2\Delta_0/kT_c = 7$. A similar value, $2\Delta_0/kT_c = 7.1$ was also obtained for a bismuth system in Ref. 44.

New measurements of Δ in $Bi_2CaSr_2Cu_2$ compound were made recently.[45] By using a procedure for fracturing a ceramic specimen, the authors could obtain tunneling characteristics approaching the ideal ones. Next they also determined Δ in a single crystal by the scanning tunneling microscope method. According to the data obtained for this compound, $2\Delta_0/kT_c = 6.6 \pm 0.4$.

Completely satisfactory tunneling characteristics were also obtained for a $Bi_{1.7}Pb_{0.3}Sr_2CaCu_2O_y$ single crystal with $T_c = 96$ K.[46] A clean crystal surface and a gold needle formed the junction. The residual current at $V \to 0$ was small and corresponded to $\beta \approx 0.1$ to 0.2 in the junctions investigated. The distance between maxima in most junctions investigated was $2\Delta_0/kT_c = 6.3$.

Unfortunately, along with characteristics that are completely satisfactory from the point of view of comparing them with typical tunneling characteristics, there are a number of publications in which recordings of junction characteristics that are similar to traditional ones are used to determine Δ. As an example, let us turn to Ref. 47, in which the author, in the investigation of a bismuth compound without detecting gap peculiarities at $eV \to 0$, compares the maxima on the $(dV/dI)(V)$ curves (instead of minima) with the peculiarities at $eV \to \Delta$. The values obtained for such characteristics hardly have a connection with Δ. We shall not dwell on other similar examples.

There are only a few tunneling investigations of the "thallium" system Tl-Ba-Ca-Cu. The gap peculiarities on the $(dI/dV)(V)$ curves obtained are barely distinguishable in Ref. 44. The authors note that, besides the peculiarities at 25 meV; a peculiarity is also visible at 5 meV, which, for example, may be connected with a low temperature phase that is present in the specimens investigated. A comparison of T_c and Δ_0 in the bismuth, thallium, and V-Ba-Cu-O$\|$ a,b-systems investigated by the authors[44] gives a similar value, $2\Delta_0/kT_c = 6.1 \pm 0.5$. A more reliable value of the gap for a $Tl_2CaBa_2Cu_2O_y$ crystal with $T_c \approx 105$ K was determined in Ref. 48 for a junction made by fracturing a specimen at 4.2 K. The characteristics obtained are reminiscent of those for a gap: $2\Delta_0/kT_c = 6.7 \pm 0.7$.

As is evident from the foregoing, research on high-temperature superconductors by the tunneling effect method is developing in two directions. In the first one, researchers are striving to obtain a junction with the best characteristics (from the point of view of approaching ideal ones), whereas the representatives of the second direction are striving to obtain junctions with stable, reproducible characteristics that often are only remotely reminiscent of tunneling ones.

The difficulty of obtaining stable tunneling junctions even for traditional superconductors is well known; as applied to oxide superconductors, the problem is made more difficult by the small correlation length, chemical instability of the surface layer, etc. it is not surprising that junctions with characteristics close to ideal ones have been obtained only in a limited number of papers, in which the value of Δ_0, and also the fact of a significant anisotropy of Δ_0 and the possibility of the variation of Δ_0 along the surface of the crystal have been reliably established. Although stable heterojunctions with reproducible characteristics have also been successfully created in a number of papers, the results obtained here do not allow an unambiguous treatment. Thus, the $(dI/dV)(V)$ relations are only remotely reminiscent of ideal tunneling characteristics (see Fig. 7), and the value of dI/dV does not approach zero at $V \to 0$, as follows from theory and a number of experiments (see Table I), but amounts to $\approx 50\%$ to 70% of the value of dI/dV at $V > \Delta/e$. The significant distortion of the characteristics in this case may be caused both by the fact that the junction is formed on a relatively large area, and that the procedures used (for example, etching the specimen) do not provide the proper cleanness for the surface of the superconductor under investigation. A similar situation occurred at the initial stage of investigating a number of traditional superconductors, for

TABLE I. Values of $\beta \to N_s(T \to 0)/N_0$ Determined from the Results of Tunneling Experiments (T), Raman Scatteing (RS), and Heat Capacity Measurements (HCM).

Material	Experimental Method	β	Reference
$La_{1,85}Sr_{0,15}CuO_4$	T	≤0,03	[10]
$Y_1Ba_2Cu_3O_{7-\delta}$	T	≈0,05	[35]
	T	≤0,1	[36]
	RS	<0,1	[64]
	HCM	?	
Bi—Sr—Ca—Cu—O	T	0,12	[41]
	RS	0,1	[66]
	HCM	≤0,05	[77]
Tl—Ba—Ca—Cu—O	T	?	
	RS	≈0,3	[68]
	HCM	≤0,05	[77]

which tunneling junctions with satisfactory characteristics were successfully created only as the result of prolonged efforts. Therefore, at the present stage of the research, reproducibility of the characteristics of heterojunctions cannot serve as evidence that they reflect the true properties of the material and not a distorted surface layer.

3. PHOTOELECTRON EMISSION

As is well known, the photoelectron spectrum enables one to determine the electron distribution near the Fermi surface if a material surface which is uncontaminated by outside impurities is used in the experiments. The advantage of this method, in comparison with tunneling, consists of the fact that direct contact with the object under investigation is not required in this case and, by changing the conditions of the experiment, one can analyze the electron spectrum in a significant vicinity of ε_F. The experiment consists of measuring the photoemission current at different angles during irradiation of the surface by photons with energies ~ 20 eV (this is usually synchrotron radiation).

When a specimen goes over into the superconducting phase, the distribution of possible electron states near the Fermi surface changes, which shows up in a dependence of the current I on the voltage E (E is measured from ε_F) near the Fermi surface. And specifically,[49] for $E < -\Delta$, in the framework of the BCS theory, the current is

$$I(E) \propto \frac{|E|}{(E^2-\Delta^2)^{1/2}}. \qquad (14)$$

Until the present, one has succeeded in detecting this effect only for single crystals of $Bi_2Sr_2CaCu_2O_y$.[49-52] This is connected with the following circumstances. To carry out the experiment successfully, it is necessary that the photoemission current in the normal phase at ε_F be large, i.e., a material possessing a high density of states near ε_F is useful. Furthermore, the crystal of the material under investigation must possess such mechanical properties that at least one of its crystallographic planes could be cleaned, for example, by cleaving in the course of the experiment. Obviously, it is necessary that the material be chemically stable and that a change of the surface layer occur fairly slowly. Since the resolving power of the equipment is limited (at present, ~ 10 meV), a superconductor with a very high critical temperature is desired.

Of the oxide superconductors known at present, crystals of the compound $Bi_2Sr_2CaCu_2O_x$, which were also used in Refs. 49 through 52, satisfy all these requirements. In the course of the experiment in the elegant Ref. 50, the surface perpendicular to the C axis of the crystal was mechanically cleaned by means of removing the surface layer. This operation was repeated every 20 minutes for the time of the entire exposure, which lasted three hours. Calibration of the instrument with respect to the position of the Fermi level was accomplished with ± 2 mV accuracy by taking spectra of copper in contact with the specimen. At large voltages from 5 V to 12 V a change of the spectrum was observed, which depended on the conditions of preparing the specimen, temperature, the averaging time-factors that are difficult to allow for. However, near ε_F in an interval ~ 120 mV below ε_F, the change of the spectrum during cooling from 105 K to 15 K is completely unambiguous and at last qualitatively agrees with the expected effect; see Fig. 11. Comparison of the experimental data with the calculation gives $\Delta_0 = 30 \pm 5$ meV, which corresponds to $2\Delta_0/kT_c = 8 \pm 1.4$. The same values of Δ_0 were obtained the same way in Refs. 29 and 51. A somewhat smaller value $\Delta_0 = 24$ meV was obtained in the research of Ref. 52. The authors note that agreement between the calculated spectrum and the experimental data leaves much room for improvement. For example, a finite current intensity at $|E| < \Delta$, which exceeds the limits of resolution of the instrument is evident in the spectrum. In the opinion of the authors, one of the possible explanations for this consists of the presence in the crystal of nonsupercon-

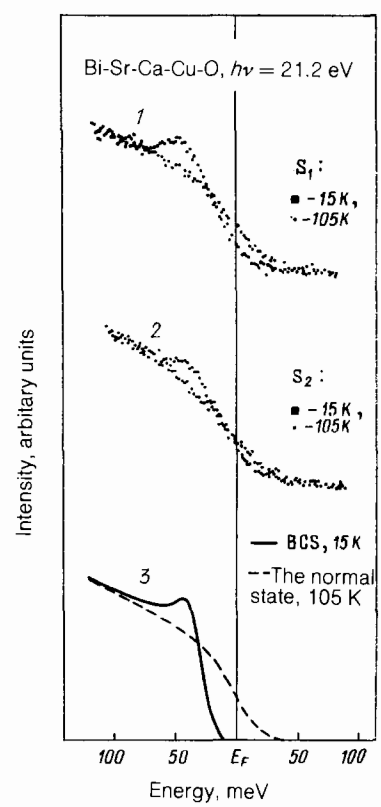

FIG. 11. Curves 1, 2 - The photoelectron current from the a,b plane of two crystals of S_1 and S_2 Bi-Sr-Ca-Cu-O in the normal and superconducting states at $T = 105$ K and 15 K. Curves 3 are calculations of the variation of current in the superconducting (the solid curve) and normal (the dashed curve) phases.[47]

ducting inclusions between the CuO layers. The angle of observation of the photoelectrons was varied to check this in the paper. This only led to variation of the amplitudes of the peculiarities without variation of their relative intensities.

This experiment is an interesting new approach to studying the properties of superconductors, which can give valuable information about the details of the electron structure of oxide superconductors near ε_F,[53] in particular, for example, it will enable one to determine the effective mass of the current carriers from the $\varepsilon(K)$ relation.

The methods of tunneling spectroscopy and photoelectron emission enable one to determine in a direct manner the width of the gap in the excitation spectra of superconductors. The relative accuracy of the determination of Δ_0 in the tunneling method is several percent, and it is 20% to 30% at present in the photoelectron emission procedure.

Besides these direct methods for measuring the value of Δ_0, a number of indirect methods are used.

4. OPTICAL METHODS

Optical research on the energy spectrum of high-temperature superconductors is developing in two directions. The first in the traditional investigation of the absorption or reflection of light in the infrared region. This method is based on the fact that in a metal for which the excitations at $T \ll T_c$ possess a gap, only phonons with energies ε that are sufficient to generate this excitation, i.e., those with energies greater than $2\Delta_0$, are absorbed. As a consequence of this, at $T \ll T_c$ the spectrum of the absorption of light by electrons must have a threshold whose location in energy corresponds to $2\Delta_0$. This method was used with success in investigating traditional superconductors. The experimental difficulty in carrying out this method is connected with the fact that, in the normal state at $T < T_c$, the absorption in the general case also depends on the frequency of the incident light.

The other direction is connected with the study of the frequency shift of light scattered by electrons. A change of the distribution in energy of the excitations in a superconductor leads to a corresponding change of the distribution in frequency of amplitudes for the light scattered by electrons. And specifically, the amplitude of the scattered light with a frequency shift $\Delta\omega$ must reflect the presence of normal excitations also in the case of a superconductor with a finite value for the energy gap, which must be vanishingly small if $T \ll T_c$. In superconductors with $T_c \sim 10$ K this effect is evidently beyond the limits of experimental capabilities,[54] since the amplitudes of the light scattered by electrons also in the normal phase are small at $\Delta\omega \to 0$. In the case of superconductors with higher critical temperatures, this effect becomes observable.

4.1.

The first research on infrared absorption carried out on yttrium and lanthanum polycrystals indicated mainly that $2\Delta_0/kT_c \sim 3$ in these compounds, i.e., it practically agrees with the value $2\Delta_0/kT_c = 3.5$ from the BCS theory, although, in a number of cases, the interpretation of the experimental curves was ambiguous. One may find a review of these measurements in Ref. 55. The results of only two impressive papers that have been written recently on oxide superconductor crystals will be considered below to illustrate the situation in this region.

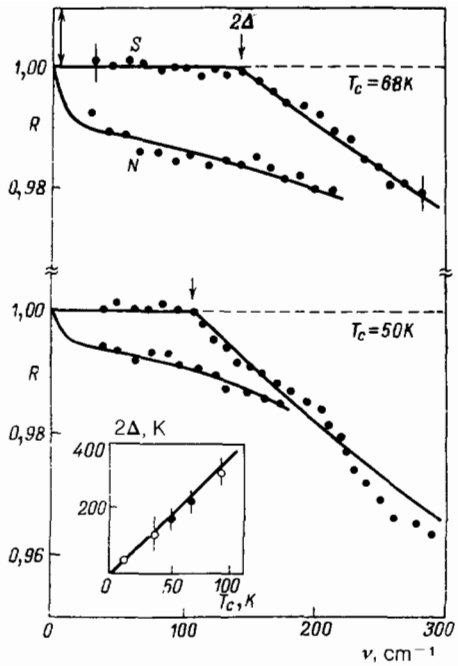

FIG. 12. The frequency dependence of the reflection of light from the a,b plane for two YBaCu crystals in the normal (N) and superconducting (S) phases. On the insert are the values of $2\Delta_0$ determined from the breaks in the curves as a function of T_c of the specimen.[52]

The frequency dependence of the reflection coefficient $R(\omega)$ for infrared radiation from the a,b plane of YBaCuO crystals with different values of T_c was investigated in Ref. 56. In the case where $\hbar\omega_1 < 2\Delta$, there is no absorption in the superconductor, and $R = 1$. The authors connect the location of the break on the $R(\omega)$ curve measured in the superconducting phase at $T < T_c$ (Fig. 12) with the value of Δ_0. According to these measurements, $2\Delta_0/kT_c = 3.5$. Not only the lack of absorption ($R = 1$ with $\sim 2\%$ accuracy) over a certain frequency interval, but also the fact that this phenomenon is observed only at temperatures $T < T_c$ is evidence in favor of the treatment of the experimental data suggested by the authors.

However, a similar investigation carried out on crystals with $T_c = 92$ K showed[57,58] that, in reality, a significant change of reflection with temperature occurs in this plane over a broader frequency interval, which corresponds to $2\Delta_0/kT_c \sim 8$. Several experimental curves from Ref. 58 are presented in Fig. 13. They show that a significant increase of the reflection R coincides with the critical temperature of the specimen. The very large value $2\Delta_0/kT_c \sim 8$ obtained in this investigation requires additional investigation from the point of view of the BCS theory. We note that one had also earlier observed in this energy range an increase of reflection during lowering of the temperature of the specimen.

It is significant that, during an investigation of the reflection of light from a plane perpendicular to the a,b plane in Ref. 58 by the same authors, a change of R in a narrow frequency interval corresponding to $2\Delta_0/kT_c \sim 3$ was detected, in which the change of reflection was observed during lowering of the temperature below T_c; the authors connect this result with the fact that a significant anisotropy of Δ_0 occurs. In particular, this result enables one to explain why just such a value of $2\Delta_0/kT_c$ was obtained earlier in most

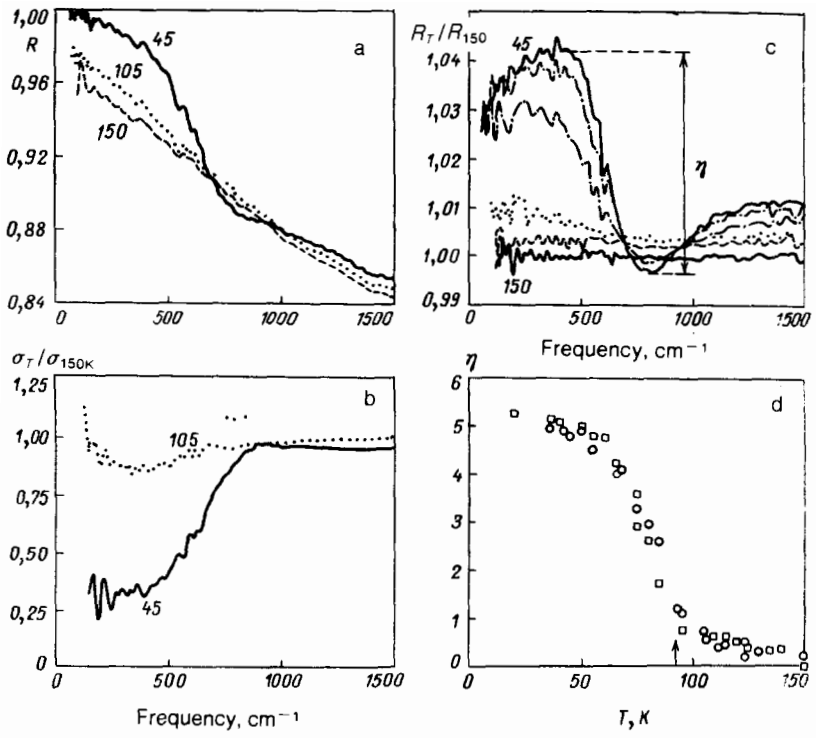

FIG. 13. a) The reflection R from the a,b plane of a $YBa_2Cu_3O_7$ crystal with $T_c = 92$ K at $T = 45$ K, 105 K, and 150 K. b) The temperature dependence of the relative change of the calculated real part of the conductance σ. c) The frequency dependence of the relative change of reflection for $T = 150$ K, 125 K, 105 K, 80 K, 55 K, and 45 K. d) The temperature dependence of the change of reflection η in the 800 cm^{-1} to 400 cm^{-1} region (two specimens).[53,54]

experiments on ceramic specimens. The point is that, during their preparation under pressure, the surface layer of the specimen turns out to be oriented perpendicular to the c axis, and thereby textured specimens were investigated in the experiments.

In conducting an investigation of reflection in $Ba_{0.6}K_{0.4}BiO_3$ and $BaPb_{0.8}Bi_{0.2}O_3$, the authors of Ref. 58 that is cited obtained $2\Delta_0/kT_c \sim 4$ for both compounds.

Recently an investigation of the infrared reflection from epitaxial films showed[59] that there are possibly two gaps in the a,b plane with $2\Delta_0/kT_c = 5.2$ and 1.9.

The problem of determining the gap by the infrared spectroscopy method cannot be regarded as finished. The experimental dependences obtained by this method are complicated and are ambiguous in their interpretation.

4.2. Electron Raman scattering

The method of the Raman scattering of light is usually used to determine the characteristic frequencies ω_0 of oscillating systems in an object being investigated with which the incident photons interact, changing their frequencies by $\Delta\omega = \omega_1 - \omega_2 = \omega_0$, where ω_1 and ω_2 are the frequencies of the incident and scattered photon, respectively. Scattering of light by electrons also occurs. A theoretical examination of this question[60,61] shows that, in a superconducting metal in the case $\xi < \delta$, where ξ is the correlation length, and δ is the depth of penetration of light into the metal, the scattering coefficient for $\Delta\omega < 2\Delta/\hbar$ is

$$\sigma(\omega) = \int_0^{\omega/2} P_s(\Delta)\left[\frac{\alpha\Delta^2}{\omega(\omega^2 - 4\Delta^2)^{1/2}} + 1\right] d\Delta, \qquad (15)$$

where $P(\Delta)$ and α are coefficients which depend on the conditions of polarization of light in the scattering process. In case the BCS theory is valid at $\hbar\Delta\omega \ll 2\Delta$, there must be no scattering by electrons in the superconducting phase at $T \to 0$.

This effect was first detected for the traditional super-

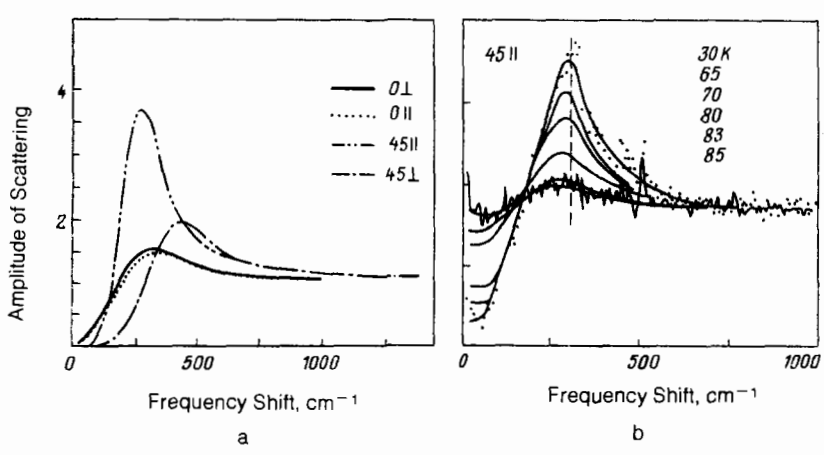

FIG. 14. a) Electron scattering of light from the a,b plane of the crystal for different polarization of light.[60] b) The temperature dependence of the amplitude of the electron Raman scattering from the a,b plane of a YBaCu crystal.[60]

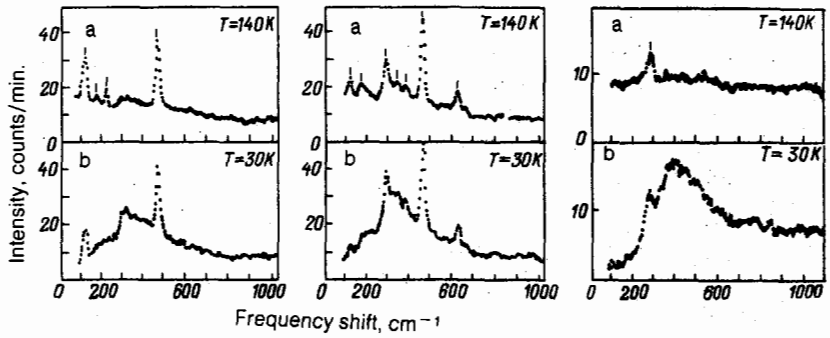

FIG. 15. Spectra of the Raman scattering from the a,b plane of a crystal of $Bi_{2.2}Sr_{1.8}CaCu_2O$ a) above T_c and b) below T_c. On the left are the polarizations of the incident and reflected light along the a axis, and b are those along the b axis. On the right are the polarizations of the incident light a) scattered along the a axis, and b) scattered along the b axis.[66]

conductors[62] Nb_3Sn and Y_3Si with relatively high critical temperatures ($T_c \sim 18$ K). The experimental curves obtained agreed satisfactorily with the theory in Ref. 60.

The use of this method in the case of oxide superconductors is complicated by the fact that several modes of lattice vibrations are usually found in the most interesting frequency interval $\Delta\omega$ and, as a consequence of this, the electron scattering spectrum is distorted by the lines of Raman light scattering by phonons. Notwithstanding this, it is clearly evident in the scattering spectrum measured at different temperatures[63] how a decrease of the amplitude of electron scattering (the background below individual lines due to phonons) occurs during lowering the temperature as $\Delta\omega \to 0$, and now it increases at $\Delta\omega \sim 2\Delta\hbar^{-1}$. One can determine from similar curves how electron scattering varies with temperature (Fig. 14).[64] It has been determined that this variation depends significantly on the polarizations of the incident and scattered light (Fig. 14a). For example, one may interpret this as a manifestation of gap anisotropy. According to this interpretation, the ratio $2\Delta_0/kT_c$ varies in the a,b plane of YBaCuO crystal from 3 ± 2 to 5.5 ± 1.6. Also see Ref. 65 for a discussion of this question.

Similar experiments are being carried out at present on bismuth and thallium systems also. The experimental results for the bismuth system are similar to those obtained for YBaCuO crystals. The change with temperature of the spectrum of the light scattering from the a,b plane of a crystal of $Bi_{2.2}Sr_{1.8}CaCu_2O_y$ for different polarizations of light is shown in Fig. 15.[66] Whereas the intensities of the phonon lines corresponding to 120, 125, 225, 295, 345, 388, 470, and 670 cm^{-1} are practically constant, the electron scattering undergoes a noticeable change upon lowering the temperature from 140 K ($T > T_c$) to 30 K ($T < T_c$). A significant decrease of the scattering amplitude is observed as $\Delta\omega \to 0$,

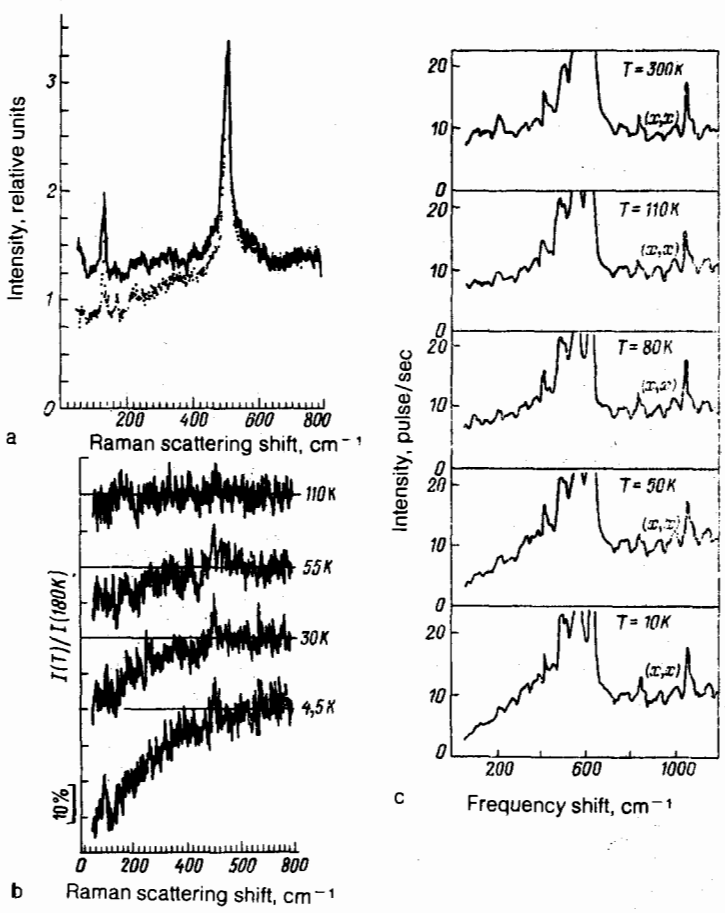

FIG. 16. a) Spectrum of the Raman scattering of light from a $Tl_2Ba_2CaCuO_8$ single crystal at $T = 180$ K (T_c) (the solid curve) and $T = 4.5$ K ($T < T_c$) (the dots). b) The temperature dependence of the $I(T)/I(180\text{ K})$. The horizontal lines are $I(T)/I(180\text{ K}) = 1$.[67] c) The temperature dependence of the amplitude of the Raman scattering from a $Tl_2Ca_2Ba_2Cu_3O_{10}$ crystal ($T_c = 105$ K) according to Ref. 68.

whereas an increase of amplitude occurs at $\Delta\omega \sim 2\Delta\hbar^{-1}$. The nature of the electron scattering variation can be described by the values $2\Delta_0/kT_c = 3.5$ for the first and second experimental configurations and $2\Delta_0/kT_c = 6.8$ for the third configuration, the same as in the YBaCuO system.

The results from Ref. 67 obtained in a thallium crystal with T_c of 110 K are presented in Fig. 16. In the opinion of the authors of the paper, the dependences obtained correspond to the value $2\Delta_0/kT_c = 5$. Later on, the authors also succeeded in detecting a dependence of Raman electron scattering on the polarization of light for these crystals. A detailed investigation of the temperature dependence for Raman electron scattering in a thallium compound crystal with $T_c \approx 110$ K[68] basically confirmed the data of Ref. 67 (see Fig. 16).

Thus, experiments on Raman electron scattering also indicate the presence of a gap peculiarity in the spectrum of the energy distribution of the excitations. However, unlike traditional ideas, the characteristics obtained in all the systems investigated differ noticeably from the characteristics which follow from the BCS model. The difference is that a noticeable contribution to scattering remains even at $\Delta\omega \to 0$. Just as in the case of the tunneling effect, this might be explained by assuming either a significant anisotropy for Δ, as a result of which the sharp boundary at $\Delta\omega \sim 2\Delta\hbar^{-1}$ is also blurred, or the presence of inclusions of the normal phase on the surface of the crystal. From an analysis of the experimental curves of Ref. 66, it follows here that the area of these "normal" sections must amount to at most only 5% to 10% of the entire area of the specimen.

5. THE BULK OF CHARACTERISTICS

In all the methods that are enumerated above for determining the value of the energy gap, the measurements were reduced to investigating the surface or near-surface characteristics of the material. As is well known, the first data on the presence of an energy gap and on its size in traditional superconductors were obtained from the results of research on the bulk properties of superconductors and, in particular, on the temperature dependence of the heat capacity and thermal conductivity of the electrons, of the magnetic characteristics of the nuclear system, etc. The possibilities for obtaining information about this energy gap based on results of determining the bulk properties of oxide superconductors will be examined in this section.

Measurements of the heat capacities of oxide superconductors were started immediately after the discovery of such compounds, on ceramic specimens at first. The presence of a linear term $C_e \propto \gamma$ T in the heat capacity as $T \to 0$, which is identified with the electron heat capacity, was established both in the compound $La_{2-x}Sr_xCuO_4$ with $0.1 < x < 0.3$, $T_c \sim 35$ K, and also in $YBaCu_3O_7$ with $T_{c\sim 90}$ K.[69]

The significance of this result is that it places in doubt the very fact of the presence of a gap in the energy spectrum of the electron excitations. Actually, as is well known,[2] in the presence of a gap, the electron excitation density near the bottom of the gap must, just like the electron heat capacity, decrease exponentially as $T \to 0$, and specifically,

$$C_e \propto e^{-\Delta/kT}; \tag{16}$$

here Δ_{min} enters into Relation (16) in the case of anisotropy of Δ. It is obvious that the presence in the heat capacity of a significant linear term of electron origin at $T \ll T_c$ contradicts Relation (16). Therefore, this result was subjected to detailed study. YBaCuO crystals were used as test objects, and measurements of the heat capacities of all the impurities, which could arise in the process of synthesizing the specimen, were carried out in addition. This analysis showed[70,71] that, with a high probability, the linear term in the heat capacity is not of electron origin. On the basis of an investigation of many $Y_xBa_{3-x}Cu_2O_{7-\delta}$ ($x = 0.9$ to 1.1) specimens, a clear correlation between the value of the linear term in the heat capacity and the contribution to the susceptibility of the specimen, which followed the Curie Law and was caused by paramagnetic impurities, was established in Ref. 72. The author of Ref. 72 assumes that the linear term in the heat capacity of YBaCuO is actually connected to a significant degree with the presence of the impurity $BaCuO_{2+x}$ in the specimens. Thereby, these papers place in doubt the presence of the linear term in the electron heat capacity in the superconducting phase.

We note that there is a Ref. 73 in which, by carrying out in $YBa_2Cu_3O_y$ crystals detailed direct measurements of the heat capacity difference ΔC for a $YBa_2Cu_3O_y$ specimen in the dielectric ($y = 6$) and superconducting ($y = 7$) modifications, the authors show that ΔC varies with temperature according to relations that are similar to those of the BCS theory, but with $2\Delta_0/kT_c = 6 \pm 0.5$. In considering this result, one must allow for the fact that it contains the assumption that the heat capacities of the lattice in the superconducting and non-superconducting modifications of the material being investigated are equal, which is not obvious, allowing for the significant difference of their lattice vibration spectra (this has been established, for example, by optical methods).

The situation is less ambiguous in bismuth and thallium compounds. Starting from the first research,[74] a linear term in the heat capacity was not detected in the bismuth compounds. The authors of Ref. 75 connected the signs of a linear term in the heat capacity of thallium compounds with the possible presence of magnetic impurities, just as in the YBaCuO compounds. Similar conclusions were also drawn in the result of investigating ceramic specimens[76] of TlCaBaCu compounds with 2223, 2212, and 221 structures.

Measurements of the heat capacities of $Bi_2Sr_2CaCu_2O_x$ and $Tl_2Ca_2Ba_2Cu_3O_y$ crystals in the 2 K to 15 K interval showed[77] that some departures from the Debye Law for the temperature dependence of the heat capacity of the lattice might be connected with the soft optical modes ($\omega_0 \sim 37$ K) and the appearance of the spin glass heat capacity of isolated magnetic impurities ($\sim 1\%$) of copper atoms. There was no linear electron term in the heat capacity within the measurement accuracy ($\gamma < 1$ J/mole K^2).

As was already indicated, the results of measurements of the temperature dependence of the heat capacities of the oxide superconductors cannot be used to determine the size of the energy gap with sufficient reliability. These measurements only enable one to obtain an upper limit estimate of the excitation density in a superconductor near the bottom of the gap by means of comparing the electron heat capacity at $T \sim T_c$ (for example, from the sudden change of the heat capacity at T_c) and estimates of the possible value of the

linear term as $T \to 0$. The results of investigating the thallium and bismuth compounds show that the excitation density at $T \ll T_c$ is about 6% of N_0, where N_0 is the excitation density in the normal phase at $T > T_c$.

As a consequence of their low specific heat capacity, the thermal conductivity $\varkappa$ of oxide superconductors is mainly determined by heat transfer by phonons. The thermal conductivity of all compounds that have been investigated up to the present in the region near T_c increases for $T < T_c$, which is obviously connected with a decrease of the scattering of phonons by electrons as a consequence of their coupling. A characteristic time for the scattering of phonons by electrons can be determined from these data.[78] This is 10^{-12} sec for YBaCuO. The determination of the gap size from the nature of the change of $\varkappa(T)$ near T_c does not appear to be reliable.

The absorption of sound in metals at $T \sim 20$ K is mainly determined by the interaction of the sound with the lattice vibrations,[79] for example, in four-phonon collisions with spin flips. Besides these processes, the interactions of sound with the soft optical modes of vibrations of oxygen and other complexes also turn out to be significant in oxide superconductors. All this leads to the situation that, until recently, one did not succeed in reliably establishing the amount and temperature dependence of the absorption of sound by conductance electrons which, as is well known,[2] could have been used to determine the energy gap.

The electrons surrounding the atomic nucleus change its nuclear magnetic resonance (NMR) frequency (the Knight shift) and lead to the appearance of a definite temperature dependence of the spin-lattice relaxation time T_1. Transition into the superconducting state is accompanied by changes of these values and enables one to obtain information about the energy gap.[2] Such measurements were carried out both on lanthanum and on yttrium systems. It was found that, from the data of Ref. 80, $2\Delta_0/kT_c = 3.6$ to 3.8 and, from the data of Ref. 81, $2\Delta_0/kT_c = 7.1$ correspond to the change of the spin-lattice relaxation time in $La_{2.85}Sr_{0.15}CuO_4$. Two times corresponding to $2\Delta_0/kT_c = 8$ and 1.2 were detected for yttrium oxide in Refs. 80 and 82. It was found out later on[83] that $2\Delta_0/kT_c = 8.3$ and 2.4 in yttrium compounds correspond to two different positions of copper in this oxide, Cu_1 and Cu_2, respectively. The fact of the noticeable change of the Knight shift during the lowering of the temperature in $YBa_2Cu_3O_7$, which satisfactorily agreed for Cu_1 atoms with the ideas of the BCS model, assuming $2\Delta_0/kT_c = 3.8$, was also established recently.[84]

However, it was assumed in analyzing these experiments that the electrons of copper atoms cause the conductance in oxide superconductors. This point of view is subject to revision at present, since the results of research on the spectra of different atoms of these compounds showed that the conductance electrons of oxides are mainly bound to the oxygen atoms. It turned out that there are two groups of electrons in oxide superconductors; conductance electrons (holes) that are bound to oxygen atoms, and electrons that are localized near copper atoms. Superconductivity is connected with the conductance electrons (holes), and the magnetic properties and their change are connected with the copper electrons. Of course these two systems are interconnected with each other; however, it is obvious that it is difficult to determine the gap size from the magnetic characteristics of the copper nuclei. The establishment of the fact of a significant (up to three orders of magnitude) decrease of the spin-lattice relaxation time $(1/T_1)$ for Cu^{63} nuclei for a change of x from 7 to 6.65 in the compound $YBa_2Cu_3O_x$ is an additional argument in favor of this idea.[85]

These ideas have become more and more popular recently (see the review in Ref. 86 with extensive additional references). A model which assumes the presence of two kinds of electrons in YBaCuO was examined qualitatively in Ref. 87. By adopting reasonable parameters, for example, $2\Delta_0/kT_c = 3.9$ for p-holes which are coupled, the authors could obtain expressions which satisfactorily describe all the experiments on the spin relaxation in YBaCuO. All this shows that additional analysis is still necessary in order to obtain information about the energy spectrum of the excitations in oxide superconductors from measurements of the characteristics of the nuclear system.

Naturally, information about the presence and size of an energy gap may be obtained not only by the methods that have been enumerated above, which cover the main field of research in this direction. Other approaches for determining the gap were also used, for example, research on the temperature dependence of the absorption of 9 GHz radiation[88] in a YBaCuO film, and the use of Andreev reflection.[89,90] These directions have not yet been extensively developed, and we shall not review them here.

6. CONCLUSION

There is evidently no basis at present to suppose that there is no energy gap in the excitation spectrum for oxide superconductors. Of course, the form of the detected gap peculiarities in a number of experimental papers is significantly different from that which we were used to seeing for traditional superconductors. First, the lack of a sharp change of the characteristics near the edge of the gap in the region of the maximum excitation density, and second, the appearance of a finite excitation density near the bottom of the band in many experimental curves are attributed to these deviations.

We shall first discuss which experimental and other causes can lead to such deviations. Next we shall compare the results of determining Δ_0 by different methods for the oxides investigated.

The lack of a sharp maximum near the edge of a gap is usually connected with the hypothesis that, in reality, the experimental results are distributed with a dispersion $\delta\Delta_0$ around an average value of Δ_0. This hypothesis seems very plausible, since a finite specimen area is usually used in the measurements and, for example, it has been demonstrated by the scanning tunneling microscope method that the size of the gap can change along the surface of a crystal (see Figs. 5 and 6). This change may be connected, for example, with a different oxygen deficit δ for $YBaCu_3O_{7-\delta}$, and in the case of attempts to use cleansing of the specimen surface by chemical etching, also with a different degree of surface contamination. At the same time, it was shown in a number of papers[23,34] that, in an individual small region of contact, the junction characteristics can be extremely sharp and can approach an ideal one (see Fig. 5). The presence of anisotropy of Δ_0 and the dependence of Δ_0 on the polarization of light,

which appears in experiments on Raman scattering, can also lead to broadening of the peculiarities.

Everything that has been said above indicates that, with a high probability, the broadening of the peculiarities near the edge of the gap is, in reality, explainable by the trivial causes that have been indicated above, and it is unnecessary to attribute it to fundamental properties of the material.

By such a method, one can explain the finite excitation density near the bottom of the gap (at $eV < \Delta$ or $\Delta\omega < \Delta\hbar^{-1}$) only if one assumes that there is a group of electrons for which a spectrum change with a gap of finite size does not arise upon the transition of the specimen into a superconducting state. Such a situation might have been connected, for example, with the presence of points or of a band on the Fermi surface where the gap size goes to zero.

Let us determine the relative concentration of normal electrons $\beta = N_s/N_0$ which remain near the bottom of the gap at $T \to 0$. The results of tunneling measurements, where

$$\beta \sim \frac{dI}{dV}\bigg|_{V\to 0}\left(\frac{dI}{dV}\bigg|_{eV>\Delta}\right)^{-1},$$

the results of investigating the amplitude of the Raman scattering of electrons A, where

$$\beta = A_{\Delta\omega\to 0}A_{\Delta\omega}^{-1} > \frac{2\Delta_0}{\hbar},$$

and the results of measuring the electron heat capacity C_e, where

$$\beta = \frac{C_e}{T}\bigg|_{T\to 0}\left(\frac{C_e}{T}\bigg|_{T>T_c}\right)^{-1}.$$

can be used for this. Values of β that have been determined by different methods were collected in Table I. We indicated only minimum values of β in Table I, since different factors leading to an increase of this value may always be present in an experiment. For example, in experiments on the tunneling effect, this may be inclusions of normal regions in the area of contact, a current of non-tunneling origin, etc. Therefore, apparently smallest value of β corresponds to the cleanest conditions for the experiment which approach those in which the true characteristics of oxide superconductors will be obtained. As is evident form the data shown in Table I, the concentration of unpaired electrons does not exceed 5% to 10% of the total number of conductance electrons in all the oxide superconductors investigated.

At least three alternative explanations may be hypothesized for this fact. First, it is not impossible that a finite value of β indicates the degree of perfection of the oxide superconductors that are prepared at present and, in reality, shows what fraction of normal inclusions there are in the specimens, for example, inclusions of a non-superconducting phase. For example, the fact of the gradual decrease of the value of β as the conditions of the experiment improve, for example, in investigations of the heat capacities of oxides, speaks in favor of this hypothesis.

Second, it is possible that, for oxide superconductors, the gap actually goes to zero on some line along the Fermi surface. The linear change of the amplitude of Raman scattering with $\Delta\omega$ at small $\Delta\omega$ speaks in favor of this hypothesis.

Finally, one may not rule out that a finite value of β indicates the specific characteristics of oxide superconduc-

TABLE II. Values of $2\Delta_0/kT_c$ in Oxide Superconductors Determined by Different Methods.

Material	$2\Delta_0/kT_c$ (...⊥ (ab)... ∥ a, b...)	Method	Reference
$Ba_1Pb_xBi_{1-x}O_3$	3,2	T	[38]
	4	IR	[54]
$Ba_{1-x}K_xBiO_3$	3,9—4,4	T	[39]
(0,4<x<0,6)	4	IR	[54]
$La_{2-x}Sr_xCuO_4$	4,95	T	[10]
$Y_1Ba_2Cu_3O_{7-\delta}$	5	T	[19]
	5,2±0,2 и 1,35±0,05	T	[34]
	5	T	[19]
	4,4±0,1	T	[24]
	...5,8...3,6...	T	[33]
	7,5 и 1,7	T	[34]
	4—6	T	[35]
	4,8	T	[36]
	3,5	IR	[50]
	7—8	IR	[53]
	...8...3...	IR	[54]
	5,2 и 1,9	IR	[55]
	7,3	RS	[59]
	5,5±1,6 и 3±2	RS	[60]
Bi—Sr—Ca—Cu—O	4,9—5,3	T	[40]
	4,5—6,5	T	[41]
	8,7	T	[42]
	7	T	[43, 44]
	6,3±0,3	T	[45]
	6,3	T	[46]
	5,5±0,6	T	[95]
	...6,2±0,3...3,3±0,3...	T	[96]
	6,8 и 3,5	RS	[62]
	8±1,4	EP	[49—51]
	7	EP	[52]
Tl—Ba—Ca—Cu—O	6,1±0,5	T	[44]
	6,9±0,8	T	[48]
	5	RS	[67]
	3,5	RS	[68]

tors. And specifically, whereas the size of the energy gap in traditional superconductors is much smaller than all the lattice vibration frequencies, for oxide superconductors, a number of vibration frequencies is smaller than the energy gap, and this could have influenced the energy distribution of the excitations. These ideas are developed in Ref. 91 as applied to Raman scattering. The fact of the Raman line displacement ω_0 upon transition into a superconducting state, which indicates the presence of a significant electron-phonon interaction, speaks in favor of this hypothesis.

At present there are insufficient data to choose between these possibilities. The author of this review thinks that one must eliminate the first, trivial explanation before constructing different theoretical models. For example, the historical course of the development of tunneling spectroscopy in traditional superconductors shows that significant deviations from standard characteristics usually turn out to be connected with a defect of the procedures used in preparing the junctions.

We now turn to the results of measuring the value of Δ_0 for different oxide superconductors. The most convincing measurements of the gap width by different methods are collected in Table II (T is the tunneling effect, IR is infrared reflection or absorption, RS is Raman scattering, and EP is electron photoemission). The values of $2\Delta_0/kT_c$ that are joined by a dotted line indicate results obtained by investigating the anisotropy of Δ_0; $\Delta_0 \perp a,b$ is on the right. As is evident from Table II, the $2\Delta_0/kT_c$ ratios for all superconductors are grouped around $2\Delta_0/kT_c = 5$ to 6. This value is significantly greater than the value $2\Delta_0/kT_c = 3.5$ of the BCS theory, but it approaches the values observed for traditional superconductors with strong bonding, such as $2\Delta_0/kT_c = 4.2$ to 4.5 for lead, 4.4 for Nb_3Sn, $2\Delta_0/kT_c = 4.6$ to 4.9 for superconducting amorphous bismuth films, etc.

As is evident from Table II, significant anisotropy of Δ_0 exists for oxide superconductors. And in particular, the value of Δ_0 parallel to the a,b, plane is more than one and a half times greater than the value of Δ_0 in a direction perpendicular to this plane. Significant anisotropy of Δ_0 was also observed earlier for traditional superconductors. Thus, for example, the ratio of $2\Delta_0/kT_c$ for tin varies from 4.3 to 2.7, depending on the crystallographic direction,[92] and thereby the oxide superconductors are not different in the amount of anisotropy of Δ_0 from traditional ones. With anisotropy of Δ_0 present, it appears to be completely natural that the value of $2\Delta_0/kT_c$ in some directions will be significantly greater than $2\Delta_0/kT_c = 3.52$, the value obtained in the standard BCS theory for the isotropic case. We note that even in the framework of an isotropic superconductor model, if one uses the consistent examination of the electron-phonon interaction carried out by Eliashberg, one can obtain the value $2\Delta_0/kT_c \approx 5$ to 6 by means of taking into account the following terms of the expansion of this quantity in T_0/ω_D[93,94] (ω_D is the characteristic phonon interaction energy), although there is apparently no basis for using this procedure in the analysis of strongly anisotropic superconductors.

Thus, as is evident from the foregoing, research on the spectra of electron excitations of oxide superconductors indicates that most of the gap characteristics of oxide high-temperature superconductors are at least qualitatively not different from those obtained earlier for traditional low-temperature superconductors. Or course this conclusion cannot serve as proof that the superconductivity in these compounds is also caused by the same electron-phonon interaction. At present, apparently one can only state that the main results of research on the energy spectrum of the excitations for the new class of superconducting compounds may be understood even in the framework of a traditional BCS type model for superconductivity.

A great many (more than 300) experimental papers are devoted to investigating the energy gap in the excitation spectrum of new oxide superconductors. However, a number of problems are still awaiting their solution. Thus, it has not yet been determined if the changes of the characteristics of a superconductor in the broad energy interval $\sim 8kT_c$ is actually connected with the gap peculiarities, or if this is a manifestation of interference effects leading, for example, to the appearance of additional peculiarities at $2\Delta_0$, etc. The problem of determining the possible density of excitations near the bottom of the gap is not finished. And finally, it has not been determined if the value of Δ_0 for perfect single crystals of oxide superconductors is a constant value or if it fluctuates along the surface. Probably these questions will be determined in the very near future.

[1]F. London, Proc. R. Soc. London Ser. A. **152**, 24 (1935).
[2]J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **106**, 168 (1956); Phys. Rev. **108**, 1175 (1957).
[3]N. N. Bogolyubov, D. N. Zubarev, and Yu. L. Tserkovnikov, Dokl. Akad. Nauk SSR **117**, 1189 (1956); [Sov. Phys. Dokl. **2**, 535 (1957)].
[4]L. P. Gor'kov, Zh. Eksp. Teor. Fiz. **34**, 735 (1958); [Sov. Phys. JETP **7**, 505 (1958)].
[5]J. O. Bednorz and K. A. Müller, Z. Phys. Kl. B **64**, 189 (1986).
[6]I. Giaever, Phys. Rev. Lett. **5**, 147, 464 (1960); Phys. Rev. **126**, 941 (1962).
[7]S. Pan *et al.*, Phys. Rev. B **35**, 7220 (1987).
[8]M. E. Hawley *et al.*, Phys. Rev. B **35**, 7224 (1987).
[9]J. R. Kirtley, C. C. Tsuei *et al.*, Phys. Rev. B **35**, 7216 (1987).
[10]A. P. Fein, J. R. Kirtley *et al.*, Phys. Rev. B. **37**, 9738 (1988).
[11]M. A. M. Gijs *et al.*, Phys. Rev. B **37**, 9837 (1988).
[12]R. S. Gonelly *et al.*, Phys. Rev. B **39**, 2261 (1989).
[13]M. C. Gallagher *et al.*, Phys. Rev. B **37**, 7846 (1988).
[14]A. Edgar, J. Phys. C **20**, L1009 (1987).
[15]I. Iguchi, Physica B + C **148**, 322 (1987).
[16]P. J. M. Van Bentum, Phys. Rev. B **36**, 843 (1987).
[17]J. R. Kirtley *et al.*, Jpn. J. Appl. Phys. **181**, 798 (1969).
[18]H. R. Zeller and I. Giaver, Phys. Rev. **181**, 798 (1969).
[19]J. R. Kirtley *et al.*, J. Vac. Sci. Tech. A **6**, 259 (1988).
[20]G. A. Emel'chenko, P. A. Kononovich, and N. A. Tulina, Fiz. Nizk. Temp. **14**, 736 (1988) [Sov. J. Low Temp. Phys. **14**, 405 (1988)].
[21]J. R. Kirtley and C. C. Tsuei, Jpn. J. Appl. Phys. **26**, 997 (1987).
[22]K. W. Nag *et al.*, Jpn. J. Appl. Phys. **26**, 993 (1987).
[23]A. P. Volodin and M. S. Khaikin, Pis'ma Zh. Eksp. Teor. Fiz. **46**, 466 (1987); [JETP Lett. **46**, 588 (1987)]; "High temperature superconductivity from Russia," in *Progress in High T_c Superconductivity* (A. I. Larkin and N. V. Zavaritsky, editors), World Scientific Publishing, Singapore, 1989, p. 201.
[24]I. V. Aleksandrov, A. P. Volodin, I. N. Makarenko, L. E. Svistov, and S. M. Stishov, Pis'ma Zh. Eksp. Teor. Fiz. **49**, 287 (1989); [JETP Lett. **49**, 327 (1989)].
[25]A. P. Volodin, B. Yu. Kotyuzhanskii, and G. A. Stepanyan, Pis'ma Zh. Eksp. Teor. Fiz. **48**, 457 (1988); [JETP Lett. **48**, 502 (1988)].
[26]E. R. Moog *et al.*, J. Low Temp. Phys. **71**, 393 (1988).
[27]M. D. Kirk *et al.*, Phys. Rev. B **35**, 8850 (1987).
[28]I. Kwo *et al.*, M²HTSC Conference July 23–28, 1989, Stanford, Calif., 1989.
[29]J. Geerk *et al.*, Z. Phys. Kl. B. **73**, 329 (1989).
[30]M. Cannovacionio *et al.*, M²HTSC Conference July 23–28, 1989, Stanford, Calif., 1989.
[31]J. R. Cavaler *et al.*, M²HTSC Conference July 23–28, Stanford, Calif., 1989.
[32]M. Burvitch *et al.*, Phys. Rev. Lett. **63**, 1008 (1989).
[33]J. S. Tsai, I. Taleuchi, *et al.*, Physica C **153**, 1385 (1988).

[34]N. V. Zavaritskii, V. N. Zavaritskii, S. V. Petrov, and A. A. Yurgens, Pis'ma Zh. Eksp. Teor. Fiz. **46**, Prilozh. 23 (1987); [JETP Lett. **46**, Suppl. 18 (1987)].
[35]V. Holm *et al.*, Z. Phys. Kl. B **69**, 173 (1987).
[36]J. Moreland *et al.*, Cryogenics **27**, 277 (1987); Phys. Rev. B **35**, 8711, 8856; Jpn. J. Appl. Phys. **26**, Suppl. 26–3, 999 (1987).
[37]R. Marsiglio and J. E. Hirsh, Physica C **159**, 153 (1989).
[38]I. Akimutsi *et al.*, Jpn. J. Appl. Phys. **26**, Suppl. 26-3, 995 (1987).
[39]J. F. Zasadzinski *et al.*, Physica C **158**, 519 (1989); M²HTSC Conference July 23–28, 1989, Stanford, Calif., 1989.
[40]T. Hasegawa *et al.*, Jpn. J. Appl. Phys. **28**, 179 (1989).
[41]S. Viera *et al.*, Phys. Rev. B **38**, 9295 (1988).
[42]H. Ikuta *et al.*, Jpn. J. Appl. Phys. **27**, L1038 (1988).
[43]M. Lee *et al.*, Phys. Rev. B **39**, 801 (1989).
[44]H. Tao *et al.*, M²HTSC Conference July 23–28, 1989, Stanford, Calif., 1989.
[45]C. Quitmann *et al.*, in *USSR-Federal Republic of Germany Bilateral Seminar*, October 29–November 10, 1989, Tallinn, USSR, 1989.
[46]Q. Muang *et al.*, Phys. Rev. B **40**, 9366 (1988).
[47]S. I. Vedeneev, I. P. Kazakov, S. N. Maksimovskii, and V. A. Stepanov, Pis'ma Zh. Eksp. Teor. Fiz. **47**, 585 (1988); [JETP Lett. **47**, 679 (1988)].
[48]J. Morland *et al.*, Appl. Phys. Lett. **55**, 1403 (1989).
[49]Y. Chang *et al.*, Phys. Rev. B **39**, 4740 (1989).
[50]J. M. Imer, F. Patthey, *et al.*, Phys. Rev. Lett. **62**, 336 (1989).
[51]R. Manzke *et al.*, Europhys. Lett. **9**, 477 (1989).
[52]C. G. Olsen *et al.*, Science **245**, 731 (1989).
[53]F. Minami, T. Kimura, *et al.*, Phys. Rev. B**39**, 4788 (1989).
[54]A. A. Abrikosov and L. A. Fal'kovskii, Zh. Eksp. Teor. Fiz. **40**, 262 (1961); [Sov. Phys. JETP **13**, 179 (1961)].
[55]T. Timusk and D. B. Tanner, in *Physical Properties of High T_c Superconductors* (D. Ginsberg, editor), World Scientific Publishing, Singapore, 1989, Ch. 7.
[56]G. A. Thomas *et al.*, Phys. Rev. Lett. **61**, 1313 (1988).
[57]Z. Schlesinger *et al.*, Physica C **153–155**, 1734 (1988).
[58]R. T. Collins, *et al.*, Phys. Rev. Lett. **63**, 422 (1989).
[59]J. Schutzmann *et al.*, Europhys. Lett. **8**, 679 (1989).
[60]M. V. Klein and S. B. Dierker, Phys. Rev. B **29**, 4976 (1984).
[61]A. A. Abrikosov and L. A. Fal'kovskii, Pis'ma Zh. Eksp. Teor. Fiz. **46**, 236 (1987); [JETP Lett. **46**, 298 (1987)].
[62]S. B. Dierker *et al.*, Phys. Rev. Lett. **50**, 853 (1983).
[63]S. L. Cooper *et al.*, Phys. Rev. B **37**, 5920 (1988).
[64]R. Hackl *et al.*, Phys. Rev. B **38**, 7133 (1988); M²HTSC Conference July 23–28, 1989, Stanford, Calif., 1989.
[65]G. Thomsen and P. Müller, in *Physical Properties of High T_c Superconductors* (D. Ginsberg, editor), World Scientific Publishing, Singapore, 1989, Ch. 8.
[66]A. Yamanaka and T. Kimura, Jpn. J. Appl. Phys. **27**, L1902 (1988).
[67]A. A. Maksimov, I. I. Tartakovskii, and V. B. Timofeev, Pis'ma Zh. Eksp. Teor. Fiz. **50**, 44 (1989); [JETP Lett **50**, 51 (1989)].
[68]M. C. Krantz, H. J. Rosen, *et al.*, Preprint Lawrence Berkeley Lab., (1989).
[69]S. von Molnar *et al.*, Phys. Rev. B **37**, 3762 (1988).
[70]J. C. Lesjaunis *et al.*, Phys. Lett. A **129**, 185 (1988).
[71]R. Kuetzler *et al.*, Solid State Commun. **65**, 1529 (1988).
[72]D. Eckert, J. Low Temp. Phys. **73**, 241 (1988).
[73]J. M. Lozan and K. A. Mizza, Physica C **153**, 1020 (1988).
[74]K. Kumagai and Y. Nakamura, Physica C **152**, 286 (1988).
[75]R. A. Fisher, S. Kim, *et al.*, Phys. Rev. B **38**, 11940 (1988).
[76]A. Junod and D. Eckert, Physica C **159**, 245 (1989).
[77]J. S. Urbach *et al.*, Phys. Rev. B **39**, 12391 (1989).
[78]N. V. Zavaritskii, A. V. Samoilov, and A. A. Yurgens, Pis'ma Zh. Eksp. Teor. Fiz. **48**, 221 (1988); [JETP Lett. **48**, 242 (1988)].
[79]W. P. Mason, Physical Acoustics; Principles and Methods, Vol. 36, Ch. 6, Academic Press, New York (1964). [Russ. Transl. Mir. M, 1968].
[80]B. A. Aleksashin, S. V. Verkhovskiy, K. N. Mikhalev, B. N. Goshchitskiy, A. N. Petrov, V. L. Kozhevnikov, A. Yu. Zuyev, and S. M. Chesnitskiy, Fiz. Met. Metalloved **64**, 392 (1987); [Phys. Met. Metallogr. **64**, 170 (1987)]; B. A. Aleksashin, S. V. Verkhovskii, B. N. Goshchitskii, A. Yu. Derevskov, A. Hu. Zuev, V. L. Kozhevnikov, V. L. Konstantinov, K. R. Krylov, A. T. Lonchakov, K. N. Mikhalev, A. N. Petrov, A. I. Ponomarov, M. B. Sadovskii, I. M. Tsidil'kovskii, V. I. Tsidil'kovskii, and S. M. Chesnitskii, Pis'ma Zh. Eksp. Teor. Fiz. **46**, Prilozh. 51 (1987); [JETP Lett. **46**, S43 (1987)].
[81]M. Lee *et al.*, Phys. Rev. B **36**, 2378 (1987).
[82]H. Seidel *et al.*, Europhys. Lett. **5**, 648 (1988).
[83]U. W. Warren *et al.*, Phys. Rev. Lett. **59**, 1860 (1987).
[84]M. Takigawa *et al.*, Phys. Rev. B **39**, 7371 (1989).
[85]K. Ishida, Y. Kitaoka, *et al.*, J. Phys. Soc. Jpn. **57**, 2897, (1988).
[86]H. Lütgemeier, in *The Eighth Intern. Conf. on Hyperfine Interactions* August 14-19, 1989, Prague.
[87]A. Yu. Zavidonov, M. V. Eremin, A. V. Egorov, V. V. Naletov, M. S. Tagirov, M. A. Teplov, and N. M. Chebotaev, Pis'ma Zh. Eksp. Teor. Fiz. **50**, 179 (1989); [JETP Lett. **50**, 201 (1989)].
[88]A. Porch *et al.*, J. Phys. F **18**, 1547 (1988).
[89]H. F. C. Hoevers *et al.*, Physica C **152**, 105 91988).
[90]P. J. M. Van Bentum *et al.*, Physica C **153**, 1378 (1988).
[91]H. Monien, Phys. Rev. Lett. **63**, 911 91989).
[92]N. V. Zavaritskii, Zh. Eksp. Teor. Fiz. **45**, 1839 (1963); [Sov. Phys. JETP **18**, 1260 (1964)]; Zh. Eksp. Teor. Fiz. **48**, 837 (1965); [Sov. Phys. JETP **21**, 557 (1965)].
[93]B. T. Geilikman and V. Z. Kresin, Fiz. Tverd. Tela **7**, 3294 (1965); [Sov. Phys. Solid State **7**, 2659 (1966)].
[94]B. Mitrovic *et al.*, Phys. Rev. B **29**, 184 (1984).
[95]A. Kussmaul *et al.*, High T_c-Update 3, No. 17 (1989).
[96]G. Briceno, high T_c-Update no. 21 (1989).

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