High-temperature superconducting ceramics (review of experimental results)[1)]

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A review is given of the experimental results on high-temperature superconducting ceramics (oxides) published in the form of papers and preprints. A brief account is given of the history of the discovery of a new classical superconducting ceramics, and the methods of their preparation as well as the main physical properties are described. The mechanism of superconductivity of these materials is discussed.

CONTENTS

1. INTRODUCTION

In a review devoted to new superconducting materials[1] Beasley and Geballe advised: "be prepared for the unexpected." The unexpected in the high-temperature superconductivity is now with us: Not only do we now have superconductors which lose their resistance completely at liquid nitrogen temperatures ($T = 77.4$ K), but there are also reports of transitions occurring at 230–250 K and even at room temperature. Undoubtedly, a very important event has occurred and the credit for the discovery belongs to many.

We shall review the experimental data on new high-temperature superconductors published in the form of papers and preprints. It is quite certain that the review will become obsolescent before it is published because of the rate at which the subject is growing. However, it is already possible to perceive the first outlines and to identify the priorities.

Two paths have led to the discovery of high-temperature superconductors. Back in 1973, chemists prepared metallic ceramics of the La_2CuO_4 type and investigated subsequently the influence of various admixtures on their properties. Physicists started from superconducting oxides: a spinel-type compound $Li_xTi_{2-x}O_4$ was discovered[2] in 1973 and the temperature of the transition to the superconducting state T_c in this compound was found to be 13.7 K; in 1974 a perovskite-type superconducting ceramic $BaPb_{1-x}Bi_xO_3$ was reported[3] and its values of T_c were up to 13 K. This discovery had to occur, but it could have happened ten years earlier. Evidently there was some psychological barrier.

Similarly, we can now have a different retrospective view on the so-called "irreproducible superconductors"[1] (see also Ref. 4) of the CuCl, CdS, and NbSi types. However, they will not be discussed here.

2. HISTORY OF THE DISCOVERY AND FIRST INVESTIGATIONS

Oxides with the tetragonal structure of the K_2NiF_4 type were found in 1958 (Ref. 5), but they have not been given serious attention right up to 1970 when their two-dimensional magnetic properties attracted real interest.[6] The metallic nature of conduction in La_2CuO_4 was discovered[7,8] in 1973. In the same year it was found[9] that the addition of strontium to La_2CuO_4 gives a compound with a phase structure of the K_2NiF_4 type. Later,[10] after the discovery of the superconductivity of ceramics based on La, it was shown that the compound La_2CuO_4 does not superconduct right down to $T = 4.2$ K.

A very important step was made in 1979 by the Soviet scientists working at the N. S. Kurnakov Institute of General and Inorganic Chemistry of the USSR Academy of Sciences.[11] They synthesized La–Ba–Cu–O, La–Sr–Cu–O, and La–Ca–Cu–O, and several other compounds showing that the temperature dependence of their resistance was of metallic nature. However, all these investigations represented only preliminary steps to the discovery of superconductivity of this class of materials.

At the end of 1986 two Swiss physicists Bednorz and Müller[12] reported superconductivity of La–Ba–Cu–O ce-

ramics with the temperature of the onset of the transition to the superconducting state $T_{co} = 35$ K. At the beginning of 1987 research groups at the Bell Telephone Laboratories (USA)[10] and at Tokyo University (Japan)[13] observed superconductivity of La–Sr–Cu–O ceramics with $T_{co} = 40$ K. The abruptness of the transition to the superconducting state exhibited by the samples used in the Bell Laboratories[10] was $\Delta T = 1.4$ K. It was reported in Ref. 13 (and also in Ref. 14) that La–Ca–Cu–O ceramics are superconductors and that $T_{co} = 25$ K. This was the end of a long era of "hydrogen" superconductors and the time arrived for "neon" superconductivity.

Single-phase samples of these ceramics were used in the investigations reported in Refs. 10, 15, and 16 and it was concluded that the superconductivity is due to a perovskite like layer phase of the K_2NiF_4 type.

Similar results on lanthanum-strontium and lanthanum-barium ceramics were obtained in February and early March 1987 by scientists at the Institute of Physics Problems of the Academy of Sciences of the USSR, Moscow Engineering-Physics Institute, Institute of Metal Physics of the Ural Branch of the Academy of Sciences of the USSR, P. N. Lebedev Physics Institute of the Academy of Sciences of the USSR, Institute of Solid-State Physics of the Academy of Sciences of the USSR, Moscow State University, Institute of Crystallography of the Academy of Sciences of the USSR, I. V. Kurchatov Institute of Atomic Energy, and several others.

A team working at the Institute of Physics of the Chinese Academy of Sciences reported in February 1987 that $T_{co} = 48.6$ K was reached for La–Sr–Cu–O ceramics and $T_{co} = 46.3$ K for La–Ba–Cu–O, which were the highest normal-pressure temperatures at this time.[17] It was reported in Ref. 15 that $T_{co} \sim 56$–70 K was obtained for one of the La–Ba–Cu–O samples which was broken and could not be reproduced; a sample of an La–Sr–Cu–O ceramic containing 0.075 at.% Sr was reported in Ref. 10 to have an extended transition with $T_{co} = 52$ K.

One should mention at this stage the work of Japanese physicists at the Kagoshima University[18] who reported superconductivity of Nb–Ge–Al–O films containing up to 20% of oxygen and characterized by T_{co} up to 44.5 K. Although Ref. 18 was published earlier than Ref. 12 and it did draw attention, it did not engender any special enthusiasm because it was not clear how the diffusion of a considerable amount of Al (in excess of 30 at.%) occurred from an Al_2O_3 substrate into the investigated films at moderate temperatures of 700–850°C. However, if one admitted some way of incorporation of Al into the film, one would have to recognize that these Japanese authors were the first to draw attention to the possibility of attainment of such high critical temperatures T_c in samples with high oxygen concentrations.

The next step was the discovery of Y–Ba–Cu–O ceramics with $T_{co} = 93$ K (Ref. 19). Samples of this system but of different composition were used at the Lebedev Physics Institute and a temperature $T_{co} = 102$ K was reported (a slow reduction of the resistance began at 115 K).[20] The latest results, the composition, and the technology used in the preparation of these ceramics were described at the V. L. Ginzburg General Moscow Seminar on March 11, 1987. The ceramic based on Y became fully superconducting in liquid

nitrogen. Therefore, the "neon" period of superconductivity was surprisingly rapidly superseded by a "nitrogen" period.

Other ceramics with the total superconductivity temperature T_{ce} exceeding the boiling point of nitrogen were soon reported.[20–22] Among these are Lu–Ba–Cu–O ceramics with $T_{ce} = 81$–85 K and a very abrupt transition characterized by $\Delta T = 1.7$ K.

The new stage of "room temperature" superconductivity began with reports of transitions deduced from the fall of the resistance which began at $T_{co} = 230$–250 K and even at room temperature. Such reports appeared in periodic journals in the USA and Japan. Very unstable signals indicating the presence of superconductivity at ordinary pressures and temperatures right up to $T = 240$ K were reported in Ref. 23 for multiphase samples which did not contain phases of the K_2NiF_4 type or of the ABO_3 perovskite type as the principal component.

3. PREPARATION METHODS

There are at present over ten different methods for the preparation of superconducting ceramics. They can be divided roughly into two groups: coprecipitation from solutions and sintering of powders (but it should be pointed out that sintering is also a stage in the coprecipitation method).

1. Coprecipitation from solutions

A mixture of solutions of nitrates was treated with a solution of NaOH in Ref. 11. The residue was washed with water in order to remove Na. The dried residue was ground and heated to 550–600 °C for 2 h, ground again, compacted into pellets (under pressure of the order of 3 kbar), and heated at 900–1000 °C in air for 60 h; the grinding and compacting stages were repeated twice again. These authors also used a variant in which the initial mixture of titrated solutions of nitrates was dried completely. A lanthanum-barium ceramic was formed in Ref. 12 by precipitation from aqueous solutions of nitrates of these metals by adding oxalic acid. A mixture of oxalates was heated to 900 °C (5 h), compacted under a pressure of 4 kbar, and heated again to 900 °C for the purpose of sintering (this was the method used in Ref. 24). Sintering of a lanthanum-barium ceramic by this method was carried out also at higher temperatures T (1100 °C, 12 h in air).[25] A mixture of solutions of appropriate acetates was treated with oxalic acid in Ref. 26. Sintering took place in an $Ar + O_2$ atmosphere at $T = 900$ °C. Precipitation from a mixture of nitrate solutions was also induced by sodium carbonate.[27] A mixture of La, Cu, and Ba (or Sr) carbonates was dried (140 °C, 8 h), heated (825 °C, 2 h), compacted, and sintered in air at 1100 °C (4 h). Sometimes this method involved an additional annealing in oxygen (200 °C, 12 h).[28]

2. Sintering of powders

A mixture of La_2O_3, CuO, and MCO_3 (M = Ca, Sr, Ba, Pb) powders was sintered in Ref. 11 to induce solid-state reactions in air at $T = 1000$–1100 °C. A similar mixture[15] was also heated in oxygen up to 900 °C (pressure 2×10^{-5} bar, 6 h). The process was repeated after grinding and then the mixture was compacted and sintered (925 °C, 24 h) at the same O_2 pressure. It was reported in Ref. 10 that a lanthanum-strontium ceramic was prepared from $La(OH)_3$,

SrCO$_3$, and CuO powders by heating at 1000 °C for several days with intermediate stages of grinding. The final mixture was compacted and annealed at 1100 °C in air (6 h). In the same investigation use was made also of annealing in a stream of O$_2$ (900 °C, 1 day) with good results. The authors of Ref. 26 heated a mixture of La$_2$O$_3$, CuO, and BaCO$_3$ in air to 900 °C and sintered it in an Ar + O$_2$ atmosphere at the same temperature T. In Ref. 13 the initial mixture consisted of La$_2$(CO$_3$)$_3$, SrCO$_3$, and CuO powders. Sintering took place in air (1000 °C). In Ref. 29 a lanthanum-barium ceramic was prepared by sintering under a pressure of 300 kbar (1000 °C, 3 h). In Ref. 30 the initial mixture consisted of La$_2$O$_3$ powders and of Cu and Sr acetates; both annealing (825 °C, 2–3 h) and sintering (1100 °C, 12–24 h) took place in air. Different variants of these methods were also described and these involved changes in the temperature and duration of annealing and in the oxygen pressure, quenching to room temperature,[31] etc.

3. Influence of preparation conditions on properties of samples

This was pointed out in the reported investigations. Under constant conditions the annealing in oxygen sometimes gave higher values of T_c and it altered the temperature dependence of the resistance as well as the value of the resistivity ρ (Ref. 10). In the first investigation of the Japanese authors[12] it was found that low annealing temperatures (500–600 °C) gave low values of T_c for a lanthanum-barium ceramic and the optimal ($\sim$950 °C) temperature and duration of annealing were found. The optimal conditions depended on the initial products and the method used to prepare the samples.

4. ELEMENTAL AND PHASE COMPOSITIONS

The main phase of superconducting lanthanum ceramics is (La$_{1-x}$M$_x$)$_2$CuO$_{4-\delta}$, where M = Ba, Sr, Ca. For example, it was found that if M is Ba, then the samples remain superconducting[16,32] in the range $0.05 \leqslant x \leqslant 0.3$. The optimal value is $x \approx 0.1$. In the case of Sr and Ca this range is at least $0.04 \leqslant x \leqslant 0.1$ (Refs. 10 and 13). The fraction of oxygen va-

cancies (represented by $\delta \gtrsim 0$) is not known accurately.

In the case of yttrium ceramics it was found that samples with high values of T_c were obtained when the compositions were (Y$_{1-x}$Ba$_x$)$_2$CuO$_4$ ($0.1 \leqslant x \leqslant 0.4$) and even Y$_{0.6}Ba_{0.4}CuO_3$ (Refs. 19 and 20).

The discovery of the superconductivity of new materials naturally raised the question which is the superconducting phase. In the first investigations the samples consisted of many phases and a clear answer to this question was not obtained. X-ray photoelectron spectroscopy and x-ray powder diffractometry were used to analyze the phase composition. Single-phase ceramic samples of (La$_{1-x}$Ba$_x$)$_2$CuO$_4$ were prepared in Ref. 16 and it was found that their structure was of the K$_2$NiF$_4$ type and also that there was a correlation between the amount of this phase and the volume fraction of the superconducting phase deduced from the change in the diamagnetic susceptibility.

The tetragonal phase of (La$_{1-x}$M$_x$)$_2$CuO$_4$ with the K$_2$NiF$_4$ structure (M = Ba, Sr, Ca, Pb) was found to have the lattice parameters $a_0 = 3.78$–3.81 Å, and $c_0 = 13.19$–13.28 Å with the axial ratio $c_0/a_0 = 3.47$–3.50 (Refs. 11 and 33). The space symmetry group of this phase is $I4/mmm$ (Ref. 34). Planes of the CuO$_6$ octahedra bound at the vertices are separated by (La, M)O layers inside which the M atoms are surrounded by nine oxygen atoms. There are two inequivalent positions of the oxygen atoms. The Cu–O bonds are strongly distorted because Cu has four nearest neighbors in the form of oxygen atoms located on a plane. It is assumed that the atoms of M stabilize the tetragonal metallic phase. Among the other phases in multiphase samples there were oxides, a perovskite-type ABO$_3$ phase, and unidentified phases. An x-ray diffractogram of a single-phase sample of (La, Ba)$_2$CuO$_4$ is shown in Fig. 1.

Yttrium-barium ceramic samples consisted of several phases.[19] Even the samples with record parameters consisted of four phases.[23] It has been suggested that the superconductivity at liquid nitrogen temperatures is not necessarily associated with phases of the K$_2$NiF$_4$ or ABO$_3$ type, but is a property of a so-far unknown phase or even of phase boundaries.
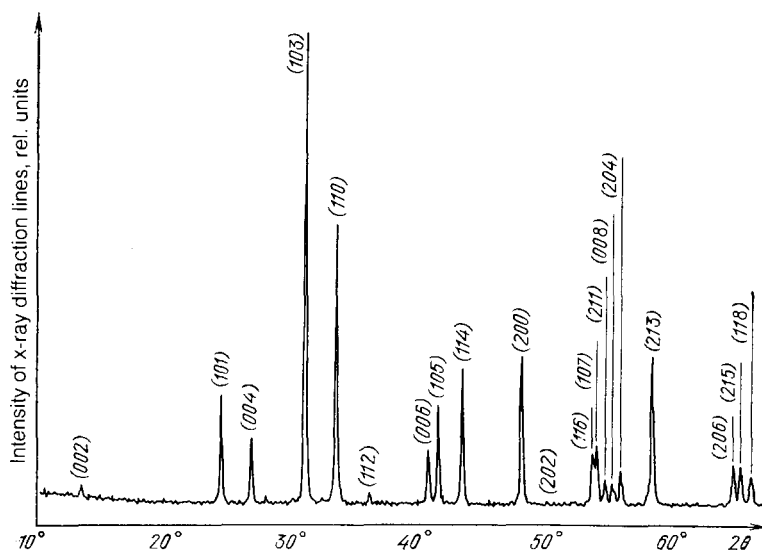

FIG. 1. Diffractogram of a single-phase sample of (La, Ba)$_2$CuO$_4$ with a phase of the K$_2$NiF$_4$ type.[16]

TABLE I. Values of critical temperatures.

Ceramic	T_{co}, K	T_c, K	T_{ce}, K	ΔT, K	Ref.
$(La_{0.925}Ca_{0.075})CuO_4$	25	19,5	18	3	13
$(La, Ba)_2CuO_4$	46,5	43	40	7	17
$(La_{1-x}Sr_x)_2CuO_4$	52	37,5	36	1,4	10
$x \approx 0,04-0,1$		45,5			17
$(Lu_{0.75}Ba_{0.25})_2CuO_4$	84	82,5	81	1,7	20
$[(Y_{0.8}Lu_{0.2})_{0.9}Ba_{0.1}]_2CuO_4$	86	82,5	79	4,5	20
$Ba_2Y_{0.75}Ss_{0.25}Cu_3O_x$	92	91	87	5	37
$(Y_{0.6}Ba_{0.4})_2CuO_4$	98	96	94	1,5	23
$(Y_{0.9}Ba_{0.1})_2CuO_4$	102	92	87	4	20
Unstable phases in ceramics based on La and Y	240—250		170		20,23

5. CRYSTAL STRUCTURE AND DENSITY

The investigated samples were polycrystalline. The published sources contain no indication that single crystals of the new ceramics were obtained. However, it has been reported[35] that superconducting single crystals and bicrystals of $BaPb_{1-x}Bi_xO_3$ were grown. Possibly single crystals of the new ceramics would be best called high-temperature superconducting oxides, as suggested by Yu. A. Osip'yan.

The theoretical density of $(La_{1-x}M_x)_2CuO_4$ is 6.4–7.2 g/cm^3, depending on the metal M and on the composition x (Ref. 11). In the case of the samples formed by coprecipitation of solutions the density can reach 97–99% of the theoretical value.[11] Sintering can produce samples with densities up to 80–85% of the theoretical value.[27,36]

Samples prepared by the ceramic technology have a granular structure which is readily observed under an electron microscope. A typical granule size is $1-10\,\mu$.

6. CRITICAL TEMPERATURES

A considerable number of papers has now been published in which high temperatures of the onset of the transition (T_{co}), the end of the transition (T_{ce}), and middle of the transition (T_c) have been achieved, and the widths of the transition to the superconducting state ΔT have been determined in the region of the most rapid variation. Table I gives the best values of these characteristics known to the author and obtained by the resistance measurements. Examples of transitions in two $(Y_{0.6}Ba_{0.4})_2CuO_4$ samples taken from Ref. 23 are reproduced in Fig. 2.

The pressure P has a strong influence on the temperature T_c of $(La_{1-x}Ba_x)_2CuO_4$ samples. It was reported in Refs. 15 and 38 that $dT_c/dP \approx 10^{-3}$ K/bar. In the case of La–Ba–Cu–O the application of pressure made it possible to reach $T_{co} = 57$ K and $T_{ce} = 40$ K. The unusually strong pressure dependence of T_c can be attributed to the possible superconductivity of the phase boundaries or some other influence of these boundaries on the properties of the system.[19] The influence of pressure on T_c of $(Y, Ba)_2CuO_4$ ceramics is much weaker. It was found in Ref. 39 that the application of $P = 20$ kbar increases the value of T_{co} for this material by just 1–1.5 K. The value of T_c increases only slightly under pressure and T_{ce} even falls. It is suggested in Ref. 39 that the weak dependence of T_c on the external pressure is associated with the existence of a strong internal ("chemical") pressure because of the small radius of the yttrium atoms.

7. MEISSNER EFFECT AND TEMPERATURE DEPENDENCE OF THE SUSCEPTIBILITY

The decisive argument in support of the superconductivity of the new materials was the observation of their diamagnetism on reduction of temperature below T_c (Refs. 15, 26, and 32). Figure 3 shows the temperature dependence of the magnetic susceptibility $\chi(T)$ reported for $(Y_{0.6}Ba_{0.4})_2CuO_4$ in Ref. 23. According to χ, the transition begins near T_c deduced from R and it is usually more extended than on the resistance scale. This may be an indication of a small amount of the high-temperature phase or of a greater depth of penetration of the field. Similar curves have been obtained for practically all the investigated samples of the various ceramics.

The low-temperature diamagnetic susceptibility χ reaches 60–80% of its ideal value $\chi_{id} = -1/4\pi$ for $(La_{1-x}M_x)CuO_4$ (Refs. 10 and 40) and 25–38% for $(Y, Ba)_2CuO_4$ (Ref. 23).
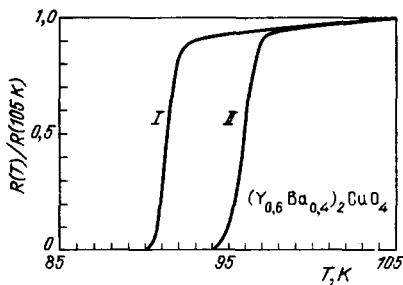

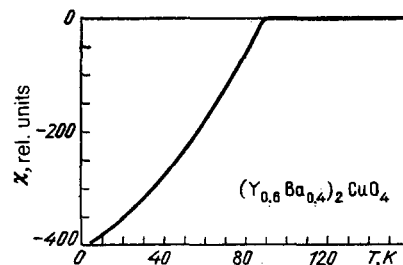FIG. 2. Transitions to the superconducting state in two samples of $(Y_{0.6}Ba_{0.4})_2CuO_4$ (Ref. 23). The resistance at a temperature T is normalized to the resistance at $T = 105$ K.

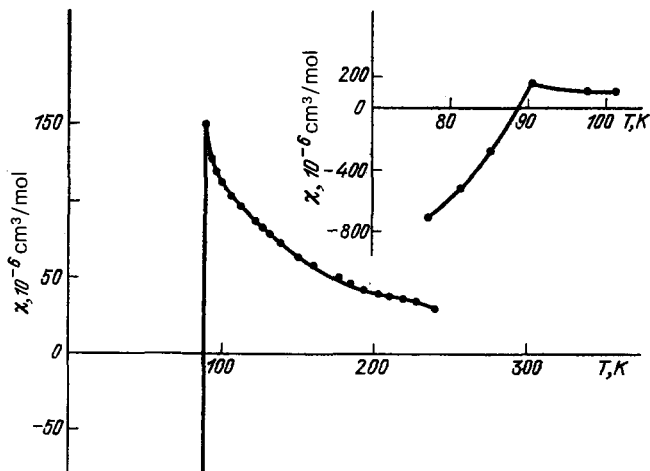FIG. 3. Temperature dependence of the magnetic susceptibility χ of $(Y_{0.6}Ba_{0.4})_2CuO_4$ (Ref. 23).

FIG. 4. Temperature dependence of χ (Ref. 20). The inset shows $\chi(T)$ near the onset of the transition.

An interesting dependence $\chi(T)$ is exhibited by the paramagnetic phase of $(Y_{0.9}Ba_{0.1})_2CuO_4$ samples[20] (Fig. 4). The rise of χ from room temperature to the onset of the transition to the diamagnetic state is greater than a factor of five.

8. TEMPERATURE DEPENDENCE OF THE RESISTANCE

The electrical resistivity ρ of $(La_{1-x}M_x)_2CuO_4$ ceramics at room temperature T_{room} is $(0.5-8) \times 10^{-3}$ $\Omega \cdot cm$, which is two orders of magnitude higher than ρ of even Nb_3Ge. In the case of yttrium-barium ceramics the resistivity is $\rho \approx (0.5 - 1) \times 10^{-1}$ $\Omega \cdot cm$ at T_{room}. The value of ρ measured at microwave frequencies is several times less than under dc conditions.

The temperature dependence of the resistance R can be semiconductor-type or metallic. The nature of the dependence $R(T)$ may be related directly to the method used in the preparation of the samples[10] (Fig. 5). Usually the metallic dependence $R(T)$ indicates a higher quality of the samples of a given composition and corresponds to higher values of T_c.

A linear dependence $R(T)$ is observed beginning from room temperature right down to T_{co}. The resistance ratio $R(300 \text{ K})/R(40 \text{ K})$ for $(La_{1-x}Sr_x)_2CuO_4$ is 2–4.

The dependence $R(T)$ of $(La_{1-x}Sr_x)_2CuO_4$ samples has a kink at $T = 120-140$ K. The value of dR/dT changes by 20% at the kink (Fig. 6).

FIG. 6. Temperature dependences of the resistance of two $(La_{2-x}Sr_x)_2CuO_4$ samples. The inset shows the curves in the region of the superconducting transition.

9. CRITICAL MAGNETIC FIELDS

Beginning from Ref. 15 it was reported that the new materials exhibit somewhat unusual dependences of the upper critical magnetic field H_{c2} on T. Although some investigations[28,41] have yielded a linear dependence of $H_{c2}(T)$ near T_c, the behavior shown in Fig. 7 for lanthanum ceramics is the more usual.[27] Clearly, in the case of both ceramics we have $d^2H_{c2}dT^2 > 0$, which distinguishes sharply the experimental dependence $H_{c2}(T)$ from that predicted on the basis of the BCS theory. Such anomalies have been reported earlier for superconducting glasses, in the case of layer superconducting systems, and for percolation superconductivity. Some of the models (for example, the model of bipolaron superconductivity[42]) predict precisely this dependence $H_{c2}(T)$.

It has also been found (as demonstrated already by the curves in Ref. 15) that the transition can split into two or become inhomogeneous in a magnetic field: The lower part
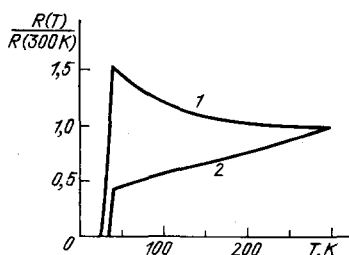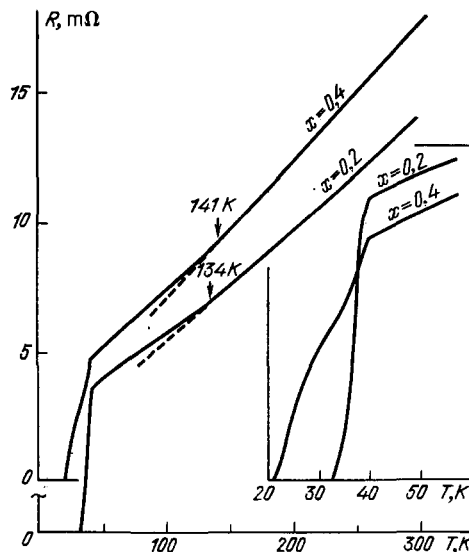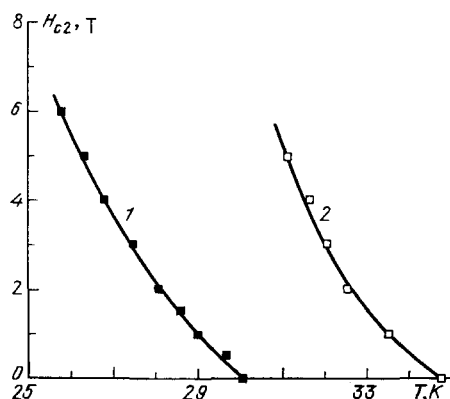

FIG. 5. Temperature dependences $R(T)$ of $(La_{0.9}Sr_{0.1})_2CuO_4$ (Ref. 10): 1) sample annealed in air; 2) sample annealed in oxygen. Here, $R(300 \text{ K})$ is the resistance at 300 K.

FIG. 7. Temperature dependences of the critical magnetic field H_{c2} of $La_{1.85}Ba_{0.15}CuO_4$ (1) and $La_{1.85}Sr_{0.15}CuO_4$ (2), plotted using the results from Ref. 27. The points on the curves were deduced from the midpoints of the transitions to the superconducting state.

of the transition can shift toward lower temperatures, whereas the upper part is little affected. Dependences of this kind have been reported for lanthanum and yttrium[19] ceramics. An inhomogeneous broadening of the transition in a magnetic field similar to that described above is predicted by the model of Ref. 43. Clearly, inhomogeneous samples containing two superconducting phases with different characteristics may exhibit similar behavior if the high-temperature phase does not shunt completely the low-temperature phase in the resistance measurements.

The value of $dH_{c2}dT$ near T_2 reaches 1.78 T/K for $(La, Ba)_2CuO_4$ (Ref. 27), 2.1 T/K for $(La, Sr)_2CuO_4$ (Ref. 36), and 3 T/K for $(Y, Ba)_2CuO_4$ (Refs. 19 and 23). A rough estimate obtained from the formula $H_{c2}(0) = 0.69T_c(dH_{c2}/dT)$ ("dirty" limit), which is known to underestimate the results, shows that in the case of $(La, Ba)_2CuO_4$ we have $H_{c2}(0) = 3.6 \times 10^5$ Oe (Ref. 27), whereas for $(La, Sr)_2CuO^4$ we have $H_{c2}(0) \approx 5.3 \times 10^5$ Oe (Ref. 36), and for Y–Ba–Cu–O the corresponding field is $H_{c2}(0) \approx 1.9 \times 10^6$ Oe (Ref. 23). Zero resistance of a sample of yttrium ceramic at 70 K was observed in a field of 5.7 T (Ref. 23). The smallness of the amount of the superconducting phase and the great depth of penetration of the field may also contribute to the observed values of the critical field.

The thermodynamic value of the critical magnetic field H_c found in Refs. 10 and 36 for $(La_{0.9}Sr_{0.1})_2CuO_4$ is 4–4.5 kOe, which is 4–5 times greater than for $BaPb_{1-x}Bi_xO_3$.

The lower critical magnetic field H_{c1} of $(La, Sr)_2CuO_4$ is estimated variously from 80–100 Oe ($T = 10$ K) given in Ref. 10 to 600 Oe ($T = 4.2$ K) given in Ref. 30; the rate of change of this field is $dH_{c1}/dT = 7.9 \pm 2$ Oe/K (Ref. 36).

10. CRITICAL CURRENT

In practically all the early investigations it was found that a small current of density 1–10 A/cm^2 reduced T_c considerably. Extrapolation to absolute zero gave values which did not exceed several tens of amperes per square centimeter. However, the presence of various defects in these samples, such as a low density (porosity), and the high resistances of the samples and contacts could prevent measurement of the true density of the critical current j_c of the superconducting phase. The measured value of j_c could be affected by the phenomena related in some way to heating.

It was reported in Ref. 36 that the samples of $(La_{0.9}Sr_{0.1})_2CuO_4$ prepared in oxygen and characterized by a density amounting to about 85% of the ideal value had a critical current density of $j_c = 6 \times 10^3$ A/cm^2 at $T = 4.2$ K in zero magnetic field H. The dependence of j on H at this temperature T in fields 10–60 kOe was very weak and in a field $H = 60$ kOe it was found that $j_c = 2 \times 10^3$ A/cm^2. At $T \approx 20$ K in zero field the critical current density was $j_c = 4 \times 10^2$ A/cm^2. Although these values of j_c are not yet comparable with the values of the critical current densities in the case of the A15 materials, they are already quite promising. After all, the samples used in Ref. 36 were far from ideal and, moreover, no optimization in the preparation conditions had been attempted in order to increase specifically the critical current density. The existence of high values of j_c in the case of $(La, Sr)_2CuO_4$ is a proof of the bulk superconductivity. An estimate of the depairing current obtained in

Ref. 36 for $(La_{0.8}Sr_{0.1})_2CuO_4$ gave 1.4×10^6 A/cm^2, which could indicate a possible limit to j_c.

11. ENERGY GAP

The presence of an energy gap, as well as its magnitude and temperature dependence are important data for the identification of the mechanism of the superconductivity of new materials. Several investigations have yielded the energy gap Δ deduced from reflection and transmission in the infrared part of the spectrum, and the first tunnel data have been obtained.

1) Experiments on infrared reflection from $(La, Sr)_2CuO_4$ and $(La, Ba)_2CuO_4$ were reported in Refs. 30 and 44. In the former case[30] the reflection was determined for a sample of $La_{1.83}Sr_{0.17}CuO_4$ illuminated normally with radiation of frequencies in the range $\nu = 10$–110 cm^{-1} (corresponding to wavelengths of 0.1–1 mm). The ratio of the reflection coefficients at $T = 2$ K (superconducting state) and $T = 80$ K (normal state) increased beginning from $\nu \approx 100$ cm^{-1}. This ratio reached its maximum value (1.2%) at $\nu \approx 60$ cm^{-1}. The value of Δ found in that investigation (using the theory of Ref. 45) was 5 ± 0.5 meV. The ratio $2\Delta/kT_c$ was found to be 3.2 ± 0.3 (k is the Boltzmann constant). The reflection from Pb was determined by way of control.

The reflection measurements reported in Ref. 44 were carried out on La–Sr–Cu–O and La–Ba–Cu–O ceramics in the frequency range $\nu = 10$–150 cm^{-1}. The energy gap was estimated from the difference between the absorptivities of a sample in the normal (at $T > T_c$) and superconducting ($T = 4.2$ K) states deduced from the experimental data. The maximum values of 2Δ obtained in this study were 38 cm^{-1} = 4.7 meV ($2\Delta/kT_c = 1.95$) for La–Ba–Cu–O and 67 cm^{-1} = 8.3 meV ($2\Delta/kT_c = 2.7$) for La–Sr–Cu–O. The gaps were considerably smaller than the values deduced from the BCS theory. The values of Δ were low possibly because of the inhomogeneity of the samples and also because of the proximity effect.

2) The value of Δ was determined in Ref. 40 from the infrared transmission measurements made on $La_{1.8}Sr_{0.2}CuO_4$ samples. These measurements were carried out on powders illuminated normally with radiation of frequencies $\nu = 20$–160 cm^{-1} ($\lambda = 60$–500 μ). Figure 8 shows the frequency dependences of the reduced difference between the transmissions $\Delta T_{SN} = (T_S - T_N)/T_N$ obtained at different temperatures (T_S and T_N are the transmissions of a sample in the superconducting state at temperatures $T < T_c$ and in the normal state at $T = 50$ K). The inset shows the temperature dependence of ΔT_{SN} (at $\nu = 86$ cm^{-1}).

The model of Refs. 46 and 47 was used to calculate the energy gap in Ref. 40 and it was found that $2\Delta = 50$ cm^{-1} and $2\Delta/kT_c = 2.5$ ($T_c = 30$ K) at $T = 10$ K. Assuming that the samples investigated by these authors had a continuous series of energy gaps and assuming that T_c was 20 K, corresponding to the middle of the variation of ΔT_{SN} (inset in Fig. 8), it was found in Ref. 40 that $2\Delta/kT_c = 3.6$. It was also shown there that the gap deduced from the transmission spectra decreased considerably on application of a magnetic field of 10 T.

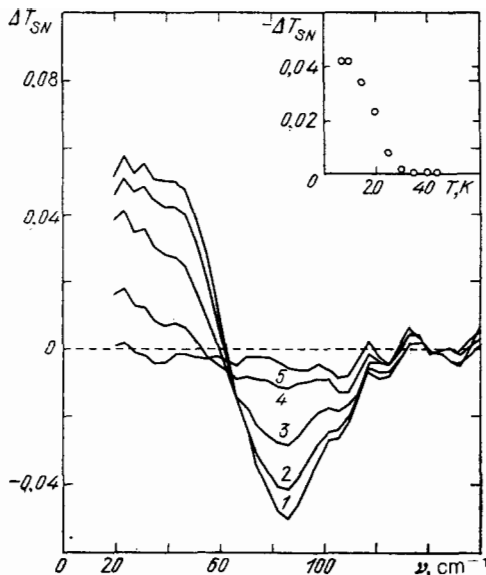3) Preliminary tunnel investigations of yttrium and lu-

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FIG. 8. Frequency dependences of the normalized difference between the transmissions exhibited by a sample of $La_{1.8}Sr_{0.2}CuO_4$ at various temperatures T (K): 1) 10; 2) 15; 3) 20; 4) 25; 5) 30. Results taken from Ref. 40. The inset shows the dependence of ΔT_{SN} on T at $\nu = 86$ cm^{-1}.

FIG. 9. Temperature dependence of the linear expansion coefficient α of $Y_{1.8}Ba_{0.2}CuO_4$.

tetium ceramics were reported in Ref. 21. The current-voltage characteristics exhibited a number of special features which disappeared at $T = T_c$. The existence of a critical current for a contact between two ceramic samples was observed up to a temperature exceeding the boiling point of nitrogen. A small (10^2 Oe) magnetic field altered the critical current of this weak superconducting link.

12. SPECIFIC HEAT AND INELASTIC NEUTRON SCATTERING

The temperature dependences of the specific heat of $La_{2-x}Sr_x CuO_4$ samples were reported in Refs. 48 and 49. In the case of samples which did not exhibit a sufficiently abrupt transition there was no jump in the specific heat ΔC at $T = T_c$ and this was accurate to within 1–2%. In the case of the samples with $x = 0.17$ it was found that $\Delta C/T_c \sim 1$ mJ·(g − atom)$^{-1}$·K^{-2}, representing $\sim 1.5\%$ of the total specific heat. Moreover, the phonon specific heat was practically the same for the samples with $T_c = 37$ and 29 K, indicating that their phonon spectra were identical. A magnetic field of 8 T shifted the specific heat jump by about 4 K toward lower temperatures. An estimate of the Debye temperature gave $\theta \approx 360$ K.

A fairly abrupt change in the specific heat in the region of T_c was reported in Ref. 22 for yttrium-barium ceramics. The temperature dependence of the specific heat exhibited an anomaly (a change in the slope) in the region of $T \approx 200$ K. Clearly, this anomaly was due to a change in the vibrational (phonon) spectrum of the sample and an increase in the Debye temperature.

Measurements of inelastic scattering of cold neutrons by $La_{1.83}Sr_{0.17}CuO_4$ revealed[49] singularities at energies 13, 25, 40, and 56 meV. The limiting frequency of the vibrational spectrum exceeded 60 meV.

13. LINEAR EXPANSION

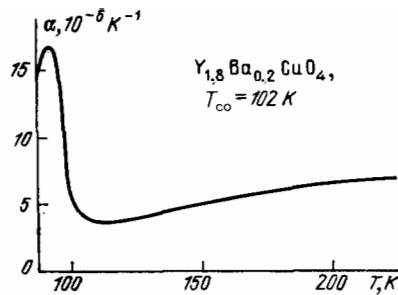The temperature dependences of the linear expansion coefficient α and of the elongation of a sample ΔL under a load of 0.02 N were determined[20] for a sample of $Y_{1.8}Ba_{0.2}CuO_4$. These dependences are plotted in Figs. 9 and 10. In the vicinity of the transition temperature the values of ΔL and α changed abruptly, which was correlated with the anomalous behavior of the susceptibility in this region. Within a narrow temperature interval the value of α changed by a factor in excess of 5. Moreover, the dependences $\alpha(T)$ and $\Delta L(T)$ also exhibited singularities at $T \approx 210$ K where the dependence $\chi^{-1}(T)$ had a clear kink.

14. HALL EFFECT AND THERMAL EMF

The positive sign of the thermal emf of ceramic La_2CuO_4 was reported some time ago.[11] The Hall coefficient and thermal emf of $La_{2-x}Sr_xCuO_4$ were found to be positive in Ref. 49 and this led to the conclusion that holes were the majority carriers. The density of holes was estimated to be within the range 10^{21}–10^{22} cm^{-3}. It was pointed out in the literature[50,51] that superconductivity was correlated with the positive value of the Hall coefficient

15. ELECTRONIC CHARACTERISTICS AND SUPERCONDUCTING STATE PARAMETERS

In this section we shall report a number of electronic characteristics, such as the mean free path l, the density of conduction electrons (charge carriers) N, the velocity of
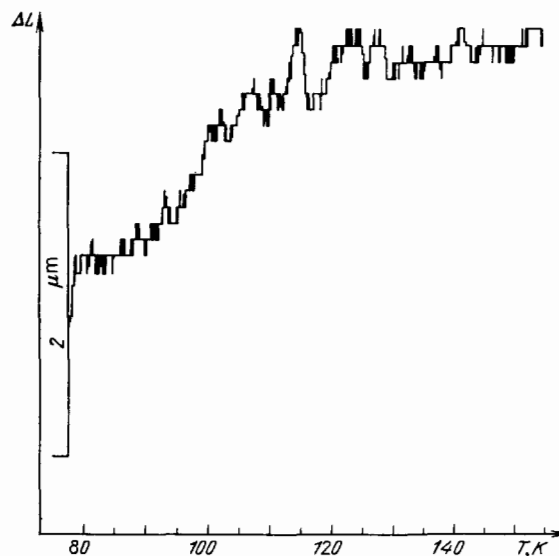

FIG. 10. Temperature dependence of the elongation of a sample of $Y_{1.8}Ba_{0.2}CuO_4$ under a load of 0.02 N (on a scale of 2 μm).

TABLE II. Properties of $(La_{1-x}Sr_x)_2CuO_4$ and $YBa_2Cu_3O_{9-\delta}$.

Property	$(La_{1-x}Sr_x)_2CuO_4$		$YBa_2Cu_3O_{9-\delta}$	$BaPb_{1-x}Bi_xO_3$	Nb_3Ge
	$x=0.075$	$x=0.1$			
T_{co}, K	41	39.5	93	—	23.4
T_c, K	33.4	36.5	92.5	10.7—12	22.1
$\rho(T_c)$, mΩ·cm	0.403	0.55	0.2—0.25	0.54—1.1	0.045
$\rho(300\,K)/\rho(T_c)$	4.3	3.1—4.1	3.6	1	2.2
j_c, A/cm²	—	$6\cdot10^3$ $(T=4,2\,K)$	$>1.1\cdot10^3$ $(T=77\,K)$	10^4—$2\cdot10^5$	$6\cdot10^6$ $(T=14\,K)$
$V_{u.c.}$, Å³	190.1	—	—	316.3 $(x=0.216)$	136
$H_{c2}(0)$, T	36	53	94—190*)	~6	33
$-\dfrac{dH_{c2}}{dT}\Big|_{T_c}$, T/K	1.51	2,1	1.5—3.0*)	0.5—0.7	2,2
H_{c1}, Oe	600**) $(T=4.2\,K)$	80—100***) $(T=10\,K)$	500 $(T=20\,K)$	—	—
$-\dfrac{dH_{c1}}{dT}$, Oe/K	—	7.9±2	7	—	—
$H_c(0)$, Oe	—	4.5±0.3	10±2	—	4,4
l, Å	$\geqslant17,2$ $(T=T_c)$ $\geqslant4.0$ $(T=300\,K)$	—	—	15 $(x=0.2)$	32
N, 10^{21} cm⁻³	~5	1	—	2.0—3.2	6.5
V_F, 10^7 cm/s	0.83—1.24	—	—	3,2	0.92
γ^*, $\dfrac{mJ}{mol.K^2}$	7.3—4,9	2.7	3—5	1.5—1.6	30
ξ_{GL}, Å	30—50	21	~22	60—79 $(x=0.25)$	26
ξ_0, Å	34—51	—	—	—	57
$\lambda_{(o)GL}$, Å	—	2500	~1000	—	890
κ	—	120	~45	—	34

*) From Ref. 23.
**) From Ref. 30.
***) From Ref. 10.

electrons on the Fermi surface v_F, a renormalized coefficient representing the electronic part of the specific heat $\gamma^* = (2\pi^2/3)k^2N^*(0)$ [$N^*(0)$ is the density of the electron states at the Fermi level], as well as several characteristics of the superconducting states, such as the Ginzburg-Landau coherence length ξ_{GL}, the depth of penetration of the field $\lambda(0)_{GL}$, the Ginzburg-Landau parameter $\varkappa$, and the BCS coherence length ξ_0, which were obtained for $(La_{1-x}Sr_x)_2CuO_4$ in Refs. 28 and 36 and for a single-phase sample of $YBa_2Cu_3O_{9-\delta}$ in Ref. 52 from measurements of T_c, H_{c2}, and H_{c1}, and also from measurements of the susceptibility and resistance. The results reported in Ref. 28 were obtained for a sample with $x = 0.075$ and those given in Ref. 36 were obtained for $x = 0.1$. The oxygen deficit δ was found to be 2.1 ± 0.05 (Ref. 52). All these characteristics are listed in Table II. This table gives also, for the sake of comparison, the corresponding characteristics for Nb_3Ge taken from Ref. 53 and for $BaPb_{1-x}Bi_xO_3$ ceramics with $x = 0.2 - 0.25$ taken from Refs. 54–57. At the beginning of this table we list the parameters of the samples [T_c, T_{co}, the resistivity $\rho(T_c)$ at $T \gtrsim T_c$, the ratio of the resistivities $\rho(300)$ at $T = 300$ K and $\rho(T_c)$, $H_{c2}(0)$, dH_{c2}/dT near T_c, H_{c1}, dH_{c1}/dT, $H_c(0)$, unit cell volume V_{uc}, and the critical current density j_c in $H = 0$] for which the electronic characteristics mentioned above were determined. In the case of a sample of $La_{1.85}Sr_{0.15}CuO_4$ there are sometimes two values in Table II: The first describes the "pure" and the other the the "dirty" limits (the authors estimated their sample to satisfy the "dirty" limit conditions). In the case of Nb_3Ge we used formulas allowing for the degree of "purity" of the sample and for the other samples we adopted the "dirty" limit.

The value of γ^* taken from Ref. 52 is in units of $mJ\cdot K^{-2}\cdot mole^{-1}Cu$. It should be pointed out that there is some scatter of the data obtained by different authors.

In estimating the density of the electron states at the Fermi level $N^*(0)$ on the basis of the electrical resistivity ρ we should bear in mind that because of inhomogeneities of a sample the value of ρ may be greatly overestimated. [Therefore, some estimates give $\gamma \sim N^*(0)$ which is 10 times less than in Table II.] It is known that in the case of granulated Ba–Pb–Bi–O samples the true value of ρ for the granules could be 10 times less than the resistivity of a sample.

The values of γ^*, i.e., of $N^*(0)$, were 2–3 times higher for $(La, Sr)_2CuO_4$ than for Ba–Pb–Bi–O ceramics (with $T_c = 10$–13 K). Therefore, assuming a somewhat stronger electron–phonon interaction for the first compound, compared with the second, we could account for $T_c = 40$ K on the basis of the BCS theory.

An attempt to estimate N was made in Ref. 36 on the assumption that all the oxygen vacancies are filled. It was then found[36] that $N = 2.1 \times 10^{21}$ cm⁻³. In the presence of O_2 vacancies the value of N fell. The annealing of samples in oxygen did indeed increase both N and T_c. The values of N deduced from the Hall effect were scattered over a fairly wide range (10^{21}–5×10^{22} cm⁻³ for lanthanum-strontium ceramics). Clearly, optical measurements would be needed to determine N accurately.

16. DISCUSSION

1) These new discoveries stimulated theoreticians to put forward various models which could account for the observed high critical temperatures and also describe other ob-

servations. An analysis of the problem can be found in the present journal in the following paper of Ginzburg and Kirzhnits.[58] Only a few comments will be made here.

There is a whole range of viewpoints that can account for the superconductivity of new materials on the basis of the usual phonon mechanism and also using several nonphonon mechanisms. From the point of view of experimentalists it is very important that some models do not explain simply the superconductivity of such ceramics, but also predict specific dependences for certain parameters.

2) Estimates obtained in several papers[28,59,60] show that in the case of lanthanum ceramics with $T_c = 30$–40 K the usual phonon mechanism of superconductivity may apply.

The high values of T_c are attributed in Ref. 59 to a "soft" phonon mode in the tetragonal structure of ceramics. The possibility of the existence of such a mode is indicated by a structural transition to the orthorhombic phase in La_2CuO_4 which occurs at $T = 250$–260 °C (Ref. 11). Moreover, a structural transition also takes place[32] when the concentration of barium is increased in $(La_{1-x}Ba_x)_2CuO_4$ ceramics. A strong interaction of electrons with such a soft mode in the case of a reasonable rise in the density of electron states $N^*(0)$ can, according to Ref. 59, explain the values of T_c observed for lanthanum ceramics by the usual electron-phonon superconductivity mechanism. A possible role of soft phonon modes in the increase in T_c of the new ceramics is mentioned also in Ref. 61. A similar conclusion is reached in Ref. 25 in a calculation of a two-dimensional conduction band associated with the existence of conducting CuO_6 layers in $(La, Ba)_2CuO_4$. It is also pointed out there that an increase in the density of electron states at the Fermi level because of a Van Hove singularity follows from the 2D model.

However, it is pointed out in Ref. 30 that the interaction of electrons solely with low-frequency phonons is insufficient to account for the observed values of Δ and T_c. In their opinion, the high values of T_c are favored by the low density of free electrons available for the screening of the electron-phonon interaction.

The properties of lanthanum-strontium ceramics are compared with the properties of the Ba–Pb–Bi–O system in Refs. 10 and 28. The fact that the density of electron states at the Fermi level is 3–5 times higher for the former system than for the latter was used to draw the conclusion that T_c ~40 K may be attained even for a constant value of the electron-phonon interaction. Moreover, it is pointed out in Ref. 61 that the properties of $La_{2-x}Ba_xCuO_4$ ceramics are similar to the properties of tungsten bronzes A_xWO_3 and $BaPb_{1-x}Bi_xO_3$.

The high values of T_c are explained in Ref. 60 by the existence of high-frequency vibrational modes in the CuO_6 octahedra and by the strong binding of electrons to these modes. Estimates obtained for the average energy of such modes in $La_{1.8}Sr_{0.2}CuO_4$ give $\hbar\omega_0 = 0.1$ eV. This corresponds to $\gamma^* \approx 3$–4 mJ·K^{-2}·mol^{-1}, a band density of the electron states $N(0) \approx 0.4$ states·eV^{-1}·atom^{-1}, and an electron-phonon interaction constant $\lambda \approx 0.4$–0.5. Then, the McMillan formula gives $T_c = 13$ K. We can obtain $T_c \approx 40$ K if $\lambda = 0.7$ and $T_c = 80$ K if $\lambda = 1$. In view of the roughness of these estimates, it is concluded in Ref. 60 that the interaction of electrons with high-frequency modes (and the large

width of the phonon spectrum) are the factors responsible for the high values of T_c of lanthanum ceramics.

Calculations of the energy band structure of $(La_{1-x}M_x)_2CuO_4$ reported in Ref. 62 showed that the properties of these materials are similar to those of $BaPb_{1-x}Bi_xO_3$. A strong coupling of electrons at the Fermi level with the "breathing" vibrational mode of the oxygen atoms can probably account for their high values of the electron-phonon interaction constant λ. The small mass and the high frequency of the oxygen atom vibrations can account for the high values of T_c exhibited by these materials. The calculations of Ref. 62 demonstrate an important role of the M atoms in ceramics, which prevent the Peierls modification of the system.

It should be pointed out that the observed dependences of certain characteristics of lanthanum ceramics [for example, $H_{c2}(T)$] do not fit the framework of the usual isotropic BCS phonon model. Therefore, it is necessary to modify this model or even invoke other mechanisms in order to explain these dependences. Some of the properties of the new ceramics are similar to the properties of superconducting glasses.[63]

3) In the case of ordinary superconductors with the phonon interaction mechanism between electrons there is an interesting correlation[1,4] between T_c and the carrier density N. Figure 11 demonstrates this correlation for the full range of N. A logarithmic scale is used in this figure to plot the maximum values of T_c representing materials with a given carrier density N. We can see that the optimal carrier density for high T_c is $N = (2$–$5) \times 10^{21}$ cm^{-3}. In this case we can expect $T_c > 40$ K. Naturally, the actual attainment of these values of T_c in a material requires not only the optimal carrier density, but also a strong electron-phonon interaction.

4) In the first investigations reporting preparation of Y–Ba–Cu–O ceramic samples with $T_{c0} = 90$–100 K it was mentioned that they consisted of several phases. In particular, it was pointed out that high values of T_c were obtained also for those samples in which the K_2NiF_4-type phase was not the main one.[23] Single-phase samples of $YBa_2Cu_3O_{9-\delta}$ ($\delta = 2.1$) were obtained subsequently[56] and
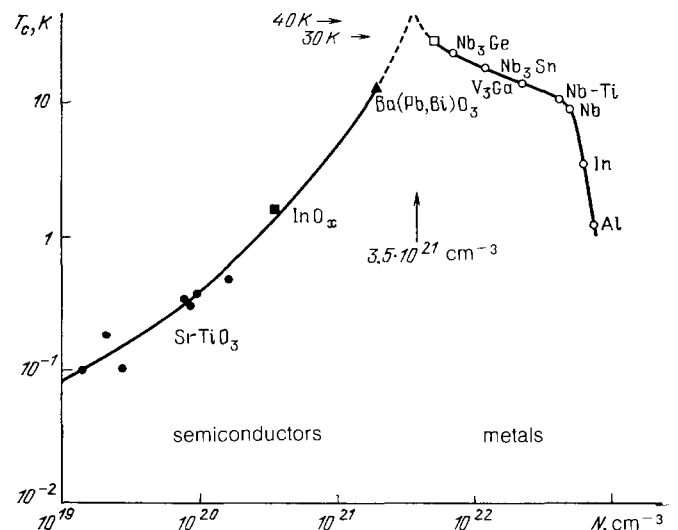

FIG. 11. Correlation between T_c and the carrier density in superconductors with the phonon mechanism.

TABLE III.

Material	(RE, Ba)CuO$_3$					
	Tm	Er	Ho	Dy	Yb	Eu
T_c, K	92	90	85	85	83	96

it was found that this phase was responsible for the high-temperature superconductivity of the Y–Ba–Cu–O system. The ABO$_3$-type phase of this composition has the structure of an orthorhombically distorted perovskite with a deficit of oxygen ($a = 3.822$ Å, $b = 3.891$ Å, $c = 11.677$ Å). Samples of this kind are characterized by $T_c = 92.5$ K (in the middle of the transition), $T_{ce} = 91$ K, and $\Delta T = 1.5$ K. The volume of the superconducting phase, deduced from expulsion of the flux, is 61% of the ideal value of $1/4\pi$.

5) In addition to the ceramics based on Y, Lu, and Sc and characterized by $T_{co} > 77.4$ K, for which data are given in Table I, other materials are now known to be superconducting in liquid nitrogen. At the conference of the American Physical Society held in New York on March 18–19, 1987, during a session on high-temperature superconducting oxides, there were reports of superconductivity in materials of the (RE, Ba)CuO$_3$ type (Table III).

The data on (Y, Ba)CuO$_3$ ($T_c = 95$ K) reported at this conference are in agreement with those known earlier. In the case of ScBa$_2$Cu$_3$O$_{9-\delta}$ the value of $T_c = 93$ K is somewhat higher than the data in Table I.

Superconductivity of Ho$_{0.246}$Ba$_{0.336}$CuO$_x$ with $T_{co} = 93$ K and $T_{ce} = 76$ K is reported in Ref. 64. In the case of a sample of Ho$_{0.234}$Ba$_{0.336}$CuO$_x$, prepared by M. L. Khidekel *et al.*, the temperatures were $T_{co} = 95$ K and $T_{ce} = 84$ K.

At sessions organized by the Divisions of General Physics and Astronomy and of Nuclear Physics S. M. Stishov (Institute of Crystallography, Academy of Sciences of the USSR) reported preparation of RE–Ba–Cu–O ceramics, where RE = Eu, Tm, Yb, Lu, characterized by $T_{co} \sim 80$–90 K. In the case of the Sm–Ba–Cu–O system it was found that $T_{co} = 40$ K and a corresponding value for La$_{1.8}$Sr$_{0.2}$CuAgO$_4$ was $T_{co} = 45$ K.

The present maximum reported value is $T_c = 102$ K (in the middle of the transition) obtained[65] for a multiphase sample of Y$_{1.2}$Ba$_{0.8}$CuO$_{4-\delta}$ ($0 \leqslant \delta \leqslant 0.4$). It is reported for this sample that $T_{co} = 125$ K and $T_{ce} = 90$ K.

6) The values $T_c \approx 90$–100 K are obviously difficult to explain by the usual phonon superconductivity mechanism, although the opposite view is held also by some authors.[60]
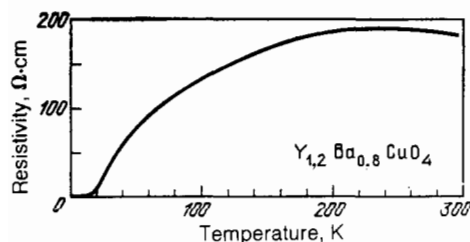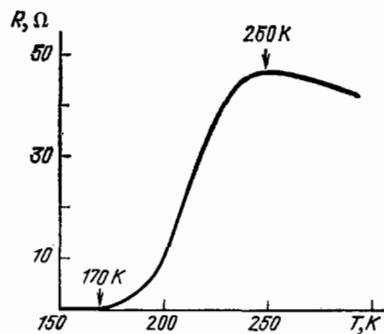

FIG. 13. Transition in yttrium ceramic beginning at 250 K (Ref. 22).

The first nonphonon mechanisms—polarization[66] and exciton[67]—were proposed back in 1964. A review of the other mechanisms can be found in Ref. 68.

A number of properties (apart from the high values of T_c) of the new high-temperature superconductors agrees with the predictions of the models proposed earlier. We shall mention here a bipolaron model[42] and a model of a narrow-gap semiconductor[43] (see also Ref. 68). Interesting conclusions on the feasibility of high-temperature superconductivity in magnetic systems can be found in Refs. 69 and 70. Enhancement of the superconductivity of thin metal films because of the interaction of electrons with resonant vibrations of atoms in a film is predicted in Ref. 71.

A new mechanism of the superconductivity of high-temperature ceramics is proposed in Ref. 72: According to this mechanism, the high values of T_c are due to an antiferromagnetic interaction in the system. A magnetic interaction manifested by the Curie-Weiss law in the case of $\chi(T)$ has indeed been reported for yttrium-barium ceramics.[20,22,52]

7) Resistive transitions beginning at $T \approx 240$ K, unstable and difficult to reproduce,[23] reported in Refs. 23 and 65 for Y–Ba–Cu–O ceramics may be associated with a very small amount of the superconducting phase or with some other physical effect (such as the Mott transition).[65] A transition of this type is illustrated in Fig. 12 (Ref. 65).

We also observed extended transitions in yttrium ceramics when the reduction in the resistance exceeded four orders of magnitude.[22,73] Two such transitions are illustrated in Figs. 13 and 14. These samples did not exhibit a diamagne-
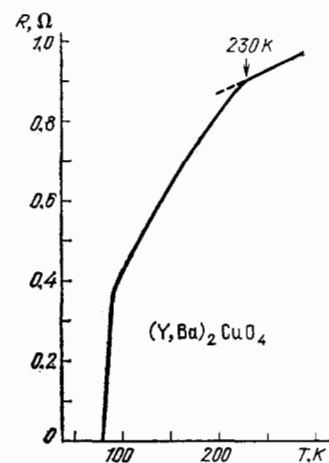

FIG. 12. Resistive transition in Y$_{1.2}$Ba$_{0.8}$CuO$_4$ beginning at $T = 240$ K (Ref. 6).

FIG. 14. Transition in Y–Ba–Cu–O ceramic beginning at $T \approx 230$ K (Ref. 73).

tic signal. The resistance increased with time during thermal cycling and eventually the transition disappeared. Before trying to understand the nature of these transitions one should first learn how to reproduce them.

It should be pointed out that abrupt changes in the resistance in nonsuperconducting barium-titanium and barium-strontium-titanium ceramics, amounting to several orders of magnitude, had been observed earlier[74] at temperatures $T = 89$–220 °C. The actual nature of these transitions has not yet been determined.

8) Numerous observations indicate that some instability is exhibited by the new high-temperature superconductors. A correlation between the high values of T_c of superconductors and the occurrence of lattice instabilities, phonon anomalies, etc., was established some time ago (see, for example, Ref. 75). In the case of the new high-temperature ceramics we can point out the following.

a) A structural phase transition occurs in La_2CuO_4 (apparently there is no stable Y_2CuO_4 phase).

b) Structural phase transitions occur also in (La, M)$_2$CuO$_4$ at, for example, high M = Ba concentrations. These transitions, like those in La_2CuO_4, occur from the tetragonal phase at high T to an orthorhombic phase at low T. The maximum values of T_c are observed for the compositions near such transitions.[32]

c) All ceramics have a limited range of concentrations in which metallic (and superconducting) phases are observed. Outside this range the resistance behaves in a semiconductor manner (although there may be no clear structural transition).

d) An interesting dependence of the resistivity of the investigated ceramics on the ratio c/a is reported in Ref. 11: these ceramics form only if $c/a \approx 3.1$ (high-resistivity materials) or $c/a \approx 3.5$ (low-resistivity materials). An instability region lies between these values.

e) Superconducting lanthanum-strontium and yttrium-barium ceramics exhibit evidence of possible structural transitions manifested in the temperature dependences of the resistance, specific heat, susceptibility, and linear expansion coefficient.[22] Singularities in the temperature dependences of these properties are observed at $T = 120$–140 K (La–Sr–Cu–O) and $T = 200$–220 K (Y–Ba–Cu–O).

f) Samples of the new materials exhibit transitions to the superconducting state which cannot be reproduced.[17] There are indications that the properties of some ceramics (particularly those with higher resistivities) vary with time. The reason for such degradation with time may be the reactions of Ba or Sr, which appear on the surfaces of the grains of ceramic samples and interact with the ambient atmosphere (O_2, H_2O). It was reported in Ref. 44 that the concentrations of these elements at grain boundaries (in a layer 50–100 Å thick) could be an order of magnitude higher than the concentrations inside the grains.

17. CONCLUSIONS

The physics of superconductivity and possibly the physics of solid state as a whole has seen an extraordinary event in the form of the discovery of really high-temperature superconductors. The rate of new reports of this kind has never been seen before since the discovery of the first superconductor. There are now ten systems which are fully super-

conducting in liquid nitrogen. The active and growing participation of Soviet and non-Soviet scientists in the study of the already discovered and search for new high-temperature superconductors is likely to lead to new discoveries. Even the materials known at present have not yet been optimized, because of the rapid growth of the subject, in respect of the preparation conditions, composition, and impurities. Undoubtedly the critical parameters (T_c, H_{c2}, j_c) will be improved, particularly by a closer approach to the boundaries of phase transitions.

Some potential applications of new superconductors in electronics are already clear. Superconducting devices and instruments made of these materials will be constructed in the near future. A very important future trend is the fabrication of high-temperature superconducting films and film structures. The first superconducting films of these materials were described at the American Physical Society conference and they were also prepared in the Soviet Union (at the Moscow Engineering-Physics Institute and at the Lebedev Physics Institute).

Undoubtedly, efforts will be made to produce high-temperature conductors for power applications in electrical engineering, magnet systems, and electrical power transmission. A new impetus will be provided to the development of superconducting computers. At present important tasks have to be carried out by physicists (identification of the superconducting phase, determination of the superconductivity mechanism, and search for new materials) and technologists (development of simple technologies for the fabrication of these materials).

Already at the dawn of the high-temperature superconductivity in the sixties and seventies W. A. Little of Stanford University put forward the idea of a superconducting memory mechanism and dreamt of artificial breeding of superconducting bacteria by selecting those with a high diamagnetism. At the time it seemed to be a fantasy. At present it is difficult to call this prediction absolutely impossible. It is probable that the most fantastic proposals for the utilization of superconductors will become reality during our generation.

[1] M. R. Beasley and T. H. Geballe, Phys. Today 37, No. 10, 60 (1984) [Russ. transl., Usp. Fiz. Nauk 148, 347 (1986)].

[2] D. C. Johnston, H. Prakash, W. H. Zachariasen, and R. Viswanathan, Mater. Res. Bull. 8, 777 (1973).

[3] A. W. Sleight, USA Patent No. 3 932 315, appl. Sept. 24, 1974, publ. Jan. 13, 1976; A. W. Sleight, J. L. Gillson, and P. E. Bierstedt, Solid State Commun. 17, 27 (1975).

[4] A. I. Golovashkin, Usp. Fiz. Nauk 148, 363 (1986) [Sov. Phys. Ups. 29, 199 (1986)].

[5] A. Rabenau and P. Eckerlin, Acta Crystallogr. 11, 304 (1958).

[6] R. J. Birgeneau, J. Skalyo Jr, and G. Shirane, J. Appl. Phys. 41, 1303 (1970).

[7] P. Ganguly and C. N. R. Rao, Mater. Res. Bull. 8, 405 (1973).

[8] T. Kenjo and S. Yajima, Bull. Chem. Soc. Jpn. 46, 1329 (1973).

[9] J. B. Goodenough, G. Demazeau, M. Pouchard, and P. Hagenmuller, J. Solid State Chem. 8, 325 (1973).

[10] R. J. Cava, R. B. van Dover, B. Batlogg, and E. A. Rietman, Phys. Rev. Lett. 58, 408 (1987).

[11] I. S. Shaplygin, B. G. Kakhan, and V. B. Lazarev, Zh. Neorg. Khim. 24, 1478 (1979) [J. Inorg. Chem. (USSR) 24, 820 (1979)].

[12]J. G. Bednorz and K. A. Müller, Z. Phys. B **64**, 189 (1986).

[13]K. Kishio, K. Kitazawa, S. Kanbe, I. Yasuda, N. Sugii, H. Takagi, S. Uchida, K. Fueki, and S. Tanaka, Chem. Lett. No. 2, 429 (1987); Preprint, Tokyo University (1987).

[14]J. G. Bednorz, K. A. Müller, and M. Takashige, Science **236**, 73 (1987); Preprint, IBM Research Laboratories, Zurich (January 14, 1987).

[15]C. W. Chu, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, and Y. Q. Wang, Phys. Rev. Lett. **58**, 405 (1987).

[16]H. Takagi, S. Uchida, K. Kitazawa, and S. Tanaka, Jpn. J. Appl. Phys. **26**, L123 (1987); Preprint, Tokyo University (1986).

[17]Z. Zhao, L. Chen, C. Cui, Y. Huang, J. Liu, G. Chen, S. Li, S. Guo, and Y. He, Preprint, Institute of Physics, Academia Sinica, Beijing (February 1987).

[18]T. Ogushi and Y. Osono, Appl. Phys. Lett. **48**, 1167 (1986).

[19]M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang, and C. W. Chu, Phys. Rev. Lett. **58**, 908 (1987).

[20]A. I. Golovashkin, O. M. Ivanenko, K. V. Mitsen, and N. E. Khramenkov, Preprint [in Russian], Lebedev Physics Institute, Academy of Sciences of the USSR, Moscow (1987).

[21]P. H. Hor, R. L. Meng, Y. Q. Wang, L. Gao, Z. J. Huang, J. Bechtold, K. Forster, and C. W. Chu, Phys. Rev. Lett. **58**, 1891 (1987); Preprint, Houston University (1987).

[22]S. Hosoya et al., Jpn. J. Appl. Phys. **26**, L325 (1987).

[23]C. W. Chu, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang, J. Bechtold, D. Campbell, M. K. Wu, J. Ashburn, and C. Y. Huang, Preprint, Houston University (1987).

[24]J. G. Bednorz, K. A. Müller, H. Arend, and H. Gränicher, Mater. Res. Bull. **18**, 181 (1983).

[25]J. D. Jorgensen, H. B. Schüttler, D. G. Hinks, D. W. Capone II, K. Zhang, M. B. Brodsky, and D. J. Scalapino, Phys. Rev. Lett. **58**, 1024 (1987); Preprint, Argonne National Laboratory (February 1987).

[26]S. Uchida, H. Takagi, K. Kitazawa, and S. Tanaka, Jpn. J. Appl. Phys. Part 2 **26**, L1 (1987).

[27]D. W. Capone II, D. S. Hinks, J. D. Jorgensen, and K. Zhang, Appl. Phys. Lett. **50**, 543 (1987); Preprint, Argonne National Laboratory (January 1987).

[28]W. K. Kwok, G. W. Crabtree, D. G. Hinks, D. W. Capone, J. D. Jorgensen, and K. Zhang, Phys. Rev. B **35**, 5343 (1987); Preprint, Argonne National Laboratory (January 1987).

[29]S. Uchida, H. Takagi, K. Kitazawa, and S. Tanaka, Jpn. J. Appl. Phys. **26**, L151 (1987); Preprint, Tokyo University (1987).

[30]D. A. Bonn, J. E. Greedan, C. V. Stager, and T. Timusk, Solid State Commun. **62**, 383 (1987); Preprint, McMaster University, Hamilton, Canada (January 1987).

[31]H. Takagi, S. Uchida, K. Kitazawa, and S. Tanaka, Preprint, Tokyo University (1987).

[32]J. G. Bednorz, M. Takashige, and K. A. Müller, Europhys. Lett. **3**, 379 (1987); Preprint, IBM Research Laboratories, Zurich (October 10, 1986).

[33]C. Michel and B. Raveau, Rev. Chem. Miner. **21**, 407 (1984).

[34]K. K. Singh, P. Ganguly, and J. B. Goodenough, J. Solid State Chem. **52**, 254 (1984).

[35]V. N. Stepankin, E. A. Protasov, A. V. Kuznetsov, and S. V. Zaĭtsev-Zotov, Pis'ma Zh. Eksp. Teor. Fiz. **41**, 23 (1985) [JETP Lett. **41**, 27 (1985)]; A. V. Kuznetsov, E. A. Protasov, and V. N. Stepankin, Preprint No. 050-86 [in Russian], Engineering-Physics Institute, Moscow (1986).

[36]A. J. Panson, G. R. Wagner, A. I. Braginski, J. R. Gavaler, M. A. Janocko, H. C. Pohl, and J. Talvacchio, Appl. Phys. Lett. **50**, 1104 (1987); Preprint, Westinghouse Research and Development Center, Pittsburgh (February 2, 1987).

[37]D. W. Murphy, S. Sunshine, R. B. van Dover, R. J. Cava, B. Batlogg, S. M. Zahurak, and L. F. Schneemeyer, Phys. Rev. Lett. **58**, 1888 (1987); Preprint, A.T.&T. Bell Laboratories, Murray Hill, N.J. (1987).

[38]C. W. Chu, P. H. Hor, R. L. Meng, L. Gao, and Z. J. Huang, Science **235**, 567 (1987).

[39]P. H. Hor, L. Gao, R. L. Meng, Z. J. Huang, Y.Q. Wang, K. Forster, J. Vassilious, C. W. Chu, M. K. Wu, J. R. Ashburn, and C. J. Torng, Phys. Rev. Lett. **58**, 911 (1987).

[40]Z. Schlesinger, R. L. Greene, J. G. Bednorz, and K. A. Müller, Phys. Rev. B**35**, 5334 (1987); Preprint, IBM Research Laboratories, Zurich (January 27, 1987).

[41]S. Uchida, H. Takagi, S. Tanaka, K. Nakao, N. Miura, K. Kishio, K. Kitazawa, and K. Fueki, Jpn. J. Appl. Phys. **26**, L196 (1987); Preprint, Tokyo University (1987).

[42]A. S. Alexandrov, J. Ranninger, and S. Robaszkiewicz, Phys. Rev. B **33**, 4526 (1986).

[43]A. I. Rusinov, D. Ch. Kat, and Yu. V. Kopaev, Zh. Eksp. Teor. Fiz. **65**, 1984 (1973) [Sov. Phys. JETP **38**, 991 (1974)].

[44]P. E. Sulewski, A. J. Sievers, S. E. Russek, H. D. Hallen, D. K. Lathrop, and R. A. Buhrman, Phys. Rev. **35**, 5330 (1987); Preprint, Cornell University (1987).

[45]D. C. Mattis and J. Bardeen, Phys. Rev. **111**, 412 (1958).

[46]W. A. Curtin and N. W. Ashcroft, Phys. Rev. B **31**, 3287 (1985).

[47]W. A. Curtin, R. C. Spitzer, N. W. Ashcroft, and A. J. Sievers, Phys. Rev. Lett. **54**, 1071 (1985).

[48]V. L. Kozhevnikov, S. M. Cheshnitskiĭ, S. A. Davydov, V. A. Fotiev, A. E. Kar'kin, A. V. Mirmel'shteĭn, A. A. Fotiev, and B. N. Goshchitskiĭ, Fiz. Met. Metalloved. **63**, 625 (1987) [Phys. Met. Metallogr. (USSR) **63**, (1987)].

[49]V. R. Galakhov, B. N. Goshchitskiĭ, V. A. Gubanov, S. A. Davydov, Yu. F. Zhuravlev, M. G. Zemlyanov, A. E. Kar'kin, V. L. Kozhevnikov, K. R. Krylov, É. Z. Kurmaev, A. T. Lonchakov, A. V. Mirmel'shteĭn, D. L. Novikov, G. Kh. Panova, P. P. Parshin, A. I. Ponomarev, A. V. Postnikov, A. F. Prekul, M. V. Sadovskiĭ, A. A. Fotiev, V. A. Fotiev, M. N. Khlopkin, I. M. Tsidil'kovskiĭ, N. A. Chernoplekov, S. M. Cheshnitskiĭ, and A. A. Shikov, Fiz. Met. Metalloved. **63**, 829 (1987) [Phys. Met. Metallogr. (USSR) **63**, (1987)].

[50]I. M. Chapnik, Phys. Lett. A **72**, 255 (1979).

[51]A. I. Golovashkin and T. I. Kuznetsova, Tr. Fiz. Inst. Akad. Nauk SSSR **151**, 3 (1984) [Proc. (Tr.) P. N. Lebedev Phys. Inst. Acad. Sci. USSR **151** (1984)].

[52]R. J. Cava, B. Batlogg, R. B. van Dover, D. W. Murphy, S. Sunshine, T. Siegrist, J. P. Remeika, E. A. Rietman, S. Zahurak, and G. P. Espinosa, Preprint, A.T.&T. Bell Laboratories, Murray Hill, N.J. (1987).

[53]A. I. Golovashkin and E. V. Pechen', Tr. Fiz. Inst. Akad. Nauk SSSR **151**, 63 (1984) [Proc. (Tr.) P. N. Lebedev Phys. Inst. Acad. Sci. USSR **151** (1984)].

[54]B. Batlogg, Physica B + C (Utrecht) **126**, 275 (1984).

[55]K. Kitazawa, S. Uchida, and S. Tanaka, Physica B + C (Utrecht) **135**, 505 (1985).

[56]K. Kitazawa, A. Katsui, A. Toriumi, and S. Tanaka, Solid State Commun. **52**, 459 (1984).

[57]M. Suzuki, Y. Hidaka, and T. Murakami, Rev. Elec. Commun. Lab. **34**, 237 (1986).

[58]V. L. Ginzburg and D. A. Kirzhnits, Usp. Fiz. Nauk **152**, 575 (1987) [Sov. Phys. Usp. **30**, 671 (1987)].

[59]S. Barišić, I. Batištić, and J. Friedel, Preprint (1987).

[60]K. H. Bennemann, Preprint, Institute for Theoretical Physics, West Berlin University (1987).

[61]J. Yu, A. J. Freeman, and J. H. Xu, Phys. Rev. Lett. **58**, 1035 (1987).

[62]L. F. Mattheiss, Phys. Rev. Lett. **58**, 1028 (1987).

[63]K. A. Müller, M. Takashige, and J. G. Bednorz, Phys. Rev. Lett. **58**, 1143 (1987); Preprint, IBM Research Laboratories, Zurich (December 1986).

[64]S. Hikami et al., Preprint, University of Tokyo (1987).

[65]C. Politis, J. Geerk, M. Dietrich, B. Obst, and H. L. Luo, J. Phys. B (in press); Preprint, Kernforschungszentrum, Karlsruhe, West Germany and University of California (1987).

[66]W. A. Little, Phys. Rev. **134**, A1416 (1964).

[67]V. L. Ginzburg, Zh. Eksp. Teor. Fiz. **47**, 2318 (1964) [Sov. Phys. JETP **20**, 1549 (1965)].

[68]V. L. Ginzburg and D. A. Kirzhnits (eds.), High-Temperature Superconductivity, Consultants Bureau, N. Y., 1982 [Russian original, Nauka, M., 1977].

[69]M. A. Savchenko and A. V. Stefanovich, *Fluctuation Superconductivity of Magnetic Systems* [in Russian], Nauka, M., 1986.

[70]A. V. Vedyaev, O. A. Kotel'nikova, M. Yu. Nikolaev, and A. V. Stefanovich, *Phase Transitions and Electronic Structure of Alloys* [in Russian], Moscow State University, 1986.

[71]V. M. Agranovich, V. E. Kravtsov, and A. G. Mal'shukov, Solid State Commun. **13**, 169 (1974).

[72]P. W. Anderson, Science **235**, 1196 (1987); Preprint, Princeton University (1987).

[73]A. I. Golovashkin, E. V. Ekimov, S. I. Krasnosvobodtsev, E. V. Pechen', and V. V. Rodin, Pis'ma Zh. Eksp. Teor. Fiz. (in press) [JETP Lett. (in press)]; Preprint [in Russian], Lebedev Physics Institute, Academy of Sciences of the USSR, Moscow (1987).

[74]H. Yanagida (ed.), *Fine Technical Ceramics* [Russ. transl. from Japanese, Metallurgiya, M., 1986].

[75]P. B. Allen, in: *Dynamical Properties of Solids. Vol. 3. Metals, Superconductors, Magnetic Materials, Liquids* (ed. by G. K. Horton and A. A. Maradudin), North-Holland, Amsterdam (1980), p.95.

Translated by A. Tybulewicz