Excess conductivity and diamagnetism in superconducting perovskite-like systems: prospects for raising the critical temperature

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Results are presented of an investigation of the electrical and magnetic properties of specimens of various compositions belonging to the R–Ba–Cu–O, Bi–Sr–Ca–Cu–O and Tl–Ba–Ca–Cu–O systems (where R are rare earth elements or yttrium). On lowering the temperature below 180 K the temperature dependences of the electrical resistance $\rho(T)$ and of the magnetic susceptibility $\chi(T)$ are found to change in most of the superconducting ($T_c > 80$ K), practically single-phase, specimens. It is shown that along with thermodynamic fluctuations, a significant contribution to $\rho(T)$ and $\chi(T)$ may come from impurity phases with values of T_c higher than those of the main phase. Their presence is confirmed by both x-ray data and measurement of the magnetic and electrical properties. Thus, for example, in some of the multiphase samples there are in the $\rho(T)$ dependence reproducible smoothened steps which extend up to 160 K. It is found that for each system the increase in T_c is accompanied by a decrease in the mean normalized distance between the layers $\bar{\varepsilon}$. An extrapolation of the $T_c(\bar{\varepsilon})$ dependences for systems with Bi and Tl shows that values of $T_c = 140$–150 K can be attained for $\bar{\varepsilon} = 0.95$. A crystallochemical analysis shows that superconducting phases with $\bar{\varepsilon} < 0.95$ should be unstable under normal conditions. However, it is very probable that they may be present in the form of impurity phases in doped and multiphase specimens.

1. INTRODUCTION

Intense investigations of metal-oxide compounds, stimulated by the discovery of high-temperature superconductivity in the system La–Ba–Cu–O (Ref. 1), led to the discovery of new superconducting phases with appreciably higher critical temperatures T_c in the systems: R–Ba–Cu–O (R is yttrium or all rare earth elements except Pm) (Refs. 2–4), Bi–Sr–Ca–Cu–O (Refs. 5–7) and Tl–Ba–Cu–O (Refs. 8–10).

All the superconducting phases with $T_c \geqslant 40$ K have quasilayer perovskite-like structures, the genesis and the possible systemization of which is discussed by Alekseevskiĭ *et al.*[11] and Santoro *et al.*[12] The highest values $T_c = 120$–130 K (Refs. 13,14), and according to reports $T_c \approx 160$ K (Ref. 15), are reached in multicomponent compounds of complicated structure, characterized by large values of the parameter c of the elementary cell.

It seemed to be of interest to elucidate how the complicating of the structure of superconducting perovskite-like phases is reflected in the change in other characteristics of the compounds, and in particular in their electrical and magnetic properties.

We give in the present work results of measuring the temperature dependences of the electrical resistivity $\rho(T)$, of the upper critical field $B_{c2}(T)$, of the magnetic susceptibility $\chi(T)$, of the magnetic moment $M(B)$, and of the tunneling current-voltage characteristics of a number of polycrystalline specimens of the systems R–Ba–Cu–O, Bi–Sr–Ca–Cu–O, and Tl–Ba–Ca–Cu–O.

2. SYNTHESIS AND PHASE COMPOSITION OF THE SPECIMENS

All the specimens studied were synthesized by the method of solid phase reaction, similar to that explained, for example, by Bednorz and Müller,[1] Wu *et al.*,[2] and LePage *et al.*[4] It was usual to choose as initial reagents the oxides R_2O_3, Bi_2O_3, Tl_2O_3, CaO, SrO, BaO_2, and CuO. A two-stage process was sometimes used in the preparation of specimens with thallium: to start with, oxides of Ca, Ba, and Cu were sintered and the product obtained was then milled, thallium or its oxide was added to it, after which the mixture was carefully ground in an agate mortar and made ready for the synthesis. In the majority of cases the synthesis of specimens was carried out in alundum crucibles. The synthesis temperature was chosen, depending on the composition of the specimens, within the limits from 1000–1450 K, while the time for synthesis varied from several minutes (for specimens of the thallium system) to several hundred hours (as, for example, in obtaining specimens of $CeBa_2Cu_3O_{6+\delta}$, when many intermediate grindings were required). Synthesis and subsequent annealing of specimens was carried out both in air and in an oxygen stream.

The phase composition of the specimens was analyzed by comparing the x-ray powder diffraction pictures obtained (DRON-2.0; Cu–K_α radiation, graphite monochromator) with data in the ASTM card index and publications available.[7,10,13,14] It follows from the x-ray data that the specimens of composition $RBa_2Cu_3O_{6+\delta}$ (R = Y, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) with $T_c = 92$–95 K, obtained after repeated grindings and subsequent heating in an oxygen stream, consist mainly of ortho I phase. Examination under an electron microscope of some of these specimens showed that they are fairly uniform. In spite of all the efforts made, an appreciable amount of impurity phases are present in superconducting specimens containing Ce, while the width of the superconducting transition curve ΔT_c for them is 10–20 K (T_c was determined from the change in the electrical resistance in the range from 0.1 to 0.9 ρ_n, where ρ_n

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is the resistance of the specimen in the normal state near T_c). A high-pressure chamber of the "torroid" type was used to obtain some specimens. Simultaneous action of high pressure (up to 80 kbar) and temperature (up to 600 K) enables compact specimens to be obtained in which there are practically no pores.

The superconducting phases in the system Bi–Sr–Ca–Cu–O identified by us can be divided into three groups:

1) $a \approx 3.83$ Å, $b \approx 3.88$ Å, and $c = 11.6$ Å;

2) $a \approx b \approx 3.82$ Å and $c = 30.5$ Å;

3) $a \approx b \approx 3.8$ Å and $c = 36.8$ Å.

The diffraction pictures of specimens of the first group with $T_c \approx 90$ K are similar to those observed for specimens of the composition $RBa_2Cu_3O_{6+\delta}$ in the case of the orthorhombic phase. Phase 2 is identical with the phase described by Hazen *et al.*[7] of composition $Bi_2Sr_2CaCu_2O_{8+\delta}$ with $T_c = 85$–90 K. Phase 3 of composition $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ corresponds to specimens in which the superconducting transition starts at 110–120 K. In addition, phases are obtained in this system with parameters $a \approx b \approx 3.8$ Å; $c = 9.46$, 24.5, 28.6, 34.5, and 39.3 Å which do not show superconductivity down to 4.2 K.

In the system Tl–Ba–Ca–Cu–O the superconducting phases with $T_c > 100$ K are characterized by the following parameters:

1) $TlBa_2Ca_2Cu_3O_{8+\delta}$ ($a = 3.85$ Å, $c = 15.88$ Å, $T_c = 123$ K),

2) $TlBa_2Ca_3Cu_4O_{10+\delta}$ ($a = 3.83$ Å, $c = 19.23$ Å, $T_c = 120$ K),

3) $Tl_2Ba_2CaCu_2O_{8+\delta}$ ($a = 3.83$ Å, $c = 29.5$ Å, $T_c = 100$–115 K),

4) $Tl_2Ba_2Ca_2Cu_3O_{10+\delta}$ ($a = 3.84$ Å, $c = 35.6$ Å, $T_c = 115$–125 K).

The parameters of the pseudotetragonal cell of all the phases agree well with published data.[10,13,14]

Superconducting specimens of the system Tl–Ba–Cu–O with $T_c \approx 90$ K consist mainly of a phase with cell parameters $a = 3.84$ Å, $b = 3.86$ Å, and $c = 11.57$ Å (Ref. 16). Attempts to replace Ba by Be led to the formation in the system Tl–Ba–Be–Cu–O of a phase with parameters $a = 3.87$ Å, and $c = 23.24$ Å (Ref. 16), which did not go into the superconducting state down to 4.2 K.

Analysis of the diffraction pictures of some multiphase specimens with Bi and Tl shows that other phases besides those enumerated above can be present, for example a phase with cell parameters $a = 3.80$ Å and $c = 43.2$ Å, the assumed composition of which corresponds to the formula $Tl_2Ba_2Ca_3Cu_4O_{12+\delta}$.

3. TEMPERATURE DEPENDENCES OF THE ELECTRICAL RESISTIVITY AND OF THE UPPER CRITICAL FIELD

The electrical resistance $\rho(T)$ of the specimens was measured by the usual four-contact method. In order to reduce the surface resistance at the position where a contact was placed, indium or an indium-gallium eutectic was rubbed into the specimen. The temperature dependence of the upper critical field $B_{c2}(T)$ was determined from resistance curves of the superconducting transition $\rho(T)|_{B=\text{const}}$, obtained for fixed values of the magnetic field B. An appreciable fraction of the measurements of $B_{c2}(T)$ and also of the magnetic moment of the specimens $M(B)$ was carried out in fields up to 14 T at the International Laboratory of High Magnetic Fields and Low Temperatures (Wroclaw, Poland).

Typical temperature dependences $\rho(T)$ of polycrystalline specimens are shown in Fig. 1 for three different systems: R–Ba–Cu–O, Bi–Sr–Ca–Cu–O, and Tl–Ba–Ca–Cu–O. Specimens of composition $RBa_2Cu_3O_{6.9}$ (apart from R = Ce) differ from specimens of the other systems in the narrower superconducting transition curves ($\Delta T_c \leqslant 2$ K) and their broadening in high magnetic fields is appreciably less, which can be regarded as evidence of much higher ordering and homogeneity of the specimens. This, in particular, is confirmed by the results of studies by x-ray diffraction and electron microscopy.

On lowering the temperature from $T = 300$ K, $\rho(T)$ decreases practically linearly for the majority of the specimens studied (within the limits of accuracy of the measurements, 0.5%) over a fairly wide temperature range. Extrapolation of the linear sections is shown in Fig. 1. by dashed lines. By comparison with specimens of five-component systems with Bi and Tl, the linear sections in the $\rho(T)$ dependences for specimens of composition $RBa_2Cu_3O_{6.9}$ are more extensive. Noticeable deviations from linearity are usually observed at 60–100 K before the superconducting transition.

The high value of the derivative $\partial\rho/\partial T$ in the normal state and the great spread of the transition curves in a magnetic field for specimens with Bi and Tl lead to serious difficulties in determining the values of $B_{c2}(T)$ by using the standard criteria, for example from the center of the transition curves (or at the $0.5\rho_n$ level). On the one hand this is associated with some indeterminacy in the choice of the value $\rho_n|_{B=0}$ on the $\rho(T)$ dependence, while on the other hand it is not always possible to trace the way in which $\rho_n(T,B)$ will change at temperatures appreciably below T_c, since an exceptionally high magnetic field would be required for this.

Recognizing that for practically all single-phase specimens of $RBa_2Cu_3O_{6.9}$, at temperatures 5–10 K above the start of the superconducting transition, the magnetoresistance in fields $\leqslant 20$ T does not exceed 1% (Ref. 17), it is reasonable to choose for the value of $\rho_n|_{B=0}$ that minimum value of $\rho(T,B)$ where the $\rho(T,B)|_{B=10\text{ T}}$ dependences start to deviate in ordinate by more than 1%. A similar determination of ρ_n can also be extended, as follows from the results obtained, to specimens of the five-component systems with Bi and Tl. The levels 0.1, 0.5, and 0.9 ρ_n on the transition curves $\rho(T,B)|_{B=\text{const}}$ can evidently be determined most definitely by taking account of the $\rho(T)$ curve in the linear section.[18] For this it is sufficient to draw the straight lines which start at the point of intersection of the extrapolation of the linear section of $\rho(T)$ (dashed lines in Fig. 1) with the abscissa axis and would go through the corresponding values of 0.1, 0.5, and 0.9 ρ_n (dashed-dot section in Fig. 1). Using these straight lines, it is possible to determine the values of $B_{c2}(T)$ corresponding, for example, to the criteria 0.5 and 0.9 ρ_n (Fig. 2). It follows from a comparison of the results obtained that the maximum values of the derivatives $|\partial B_{c2}/\partial T|_{0.9\rho_n} = 7$–$9$ T/K and $|\partial B_{c2}/\partial T|_{0.5\rho_n} = 3.1$–$3.5$ T/K, determined according to the criteria 0.9 and $0.5\rho_n$, observed for the most homogeneous specimens of $RBa_2Cu_3O_{6.9}$. For specimens with Bi the maximum values of the derivatives at the 0.9 and $0.5\rho_n$ levels are 6–7 T/K and 2–2.5 T/K, and for specimens with Tl they are respectively

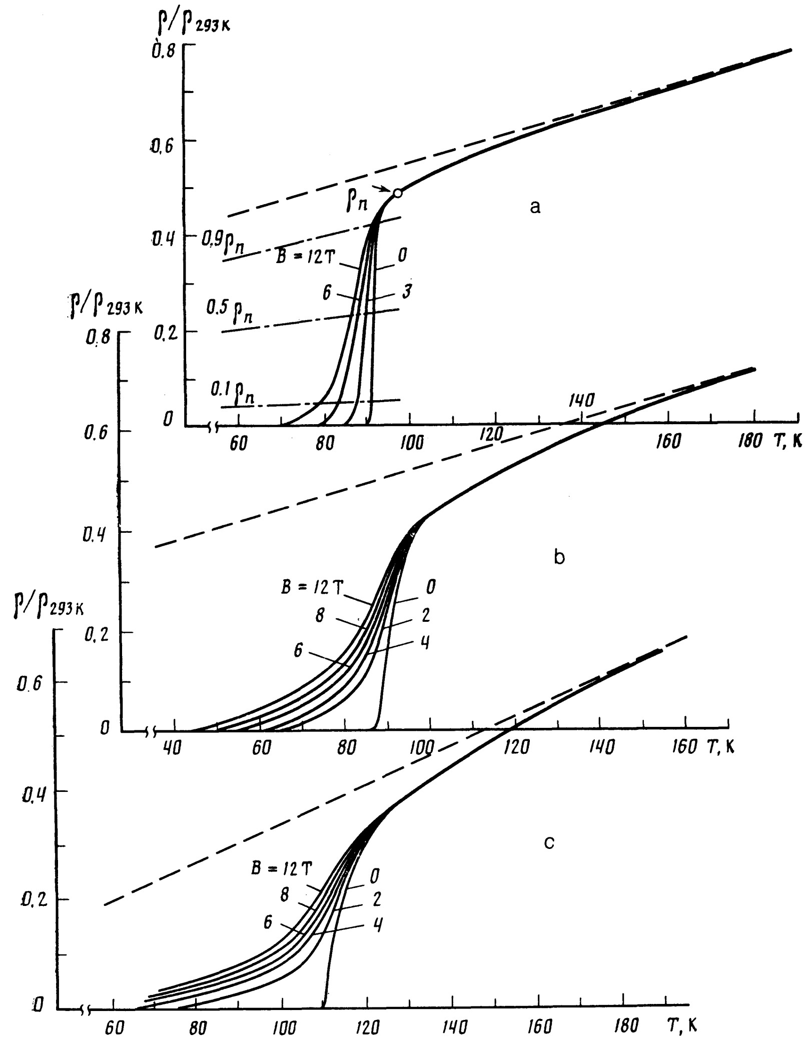

FIG. 1. Temperature dependences of the reduced electrical resistance of the specimens a) $ErBa_2Cu_3O_{6.9}$, b) $Bi_2Sr_2CaCu_2O_{8+\delta}$, and c) $Tl_2Ba_2Ca_2Cu_3O_{10+\delta}$, obtained at several values of the magnetic field $B = 0, 2, 3, 4, 6, 8,$ and 12 T. The dashed straight lines are extrapolations of the linear sections of the $\rho(T)$ dependences from the region $180 < T < 300$ K (other details are given in the text).

4–5 T/K and 1.5–1.8 T/K.

The values of the derivatives $|\partial B_{c2}/\partial T|$ for specimens with Bi and Tl correspond roughly with the results of measurements of $B_{c2}(T)$ for specimens with the 1–2–3 structure with approximately the same superconducting transition width $\Delta T = 5$–10 K (in the absence of a field). It is not impossible that with improvement in the technology of synthesis it would be possible to obtain specimens of the bismuth and thallium systems with appreciably narrower superconducting transition curves, but this would probably also lead to a noticeable increase in the curvatures of the $B_{c2}(T)$ dependences. Preliminary investigations which we carried out of the influence of annealing on the $B_{c2}(T)$ dependence showed that no appreciable change in ΔT_c and in the derivatives $\partial B_{c2}/\partial T$ takes place, although T_c can then grow somewhat.

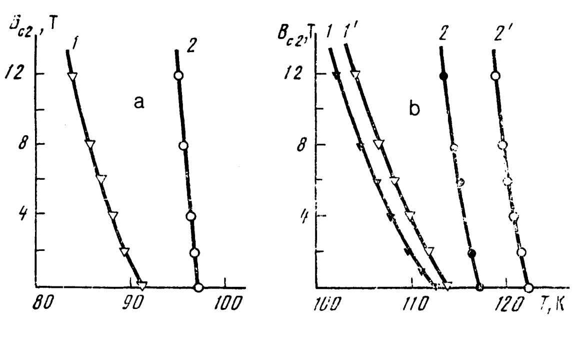

FIG. 2. Temperature dependences of the upper critical field $B_{c2}(T)$ determined from the $0.5\rho_n$ criterion (curves 1, 1′) and $0.9\rho_n$ (curves 2, 2′) for specimens: a) $Bi_2Sr_2CaCu_2O_{8+\delta}$, b) $Tl_2Ba_2Ca_2Cu_3O_{10+\delta}$, (curves 1 and 2 correspond to the initial specimen, while 1′ and 2′ have undergone an additional anneal at $T \approx 1000$ K.

The open symbols in Fig. 2b show $B_{c2}(T)$ dependences for a specimen of $Tl_2Ba_2Ca_2Cu_3O_{10+\delta}$ which underwent additional annealing at $T \approx 1000$ K for 8 h. It follows from the results obtained that even for the most homogeneous specimens of $RBa_2Cu_3O_{6.9}$ with $\Delta T_c \leqslant 1$ K the difference in the slope of the $B_{c2}(T)$ dependences, determined from the criteria 0.9 and $0.5\rho_n$, is several times greater than is observed for traditional superconductors, for example with the A-15 or Chevrel phase structures.[19] As well as inhomogeneity, an anisotropy in $B_{c2}(T)$ may lead to such a large difference in the derivatives $|\partial B_{c2}/\partial T|_{0.9\rho_n}$ and $|\partial B_{c2}/\partial T|_{0.5\rho_n}$. Since specimens of all three systems have a quasilayer structure, the anisotropy of the upper critical field can be estimated from the magnitude of the spread of the superconducting transition curves for directions perpendicular and parallel to the c axis:

$$B_{c2\perp}(T)/B_{c2\parallel}(T) \approx 2|\partial B_{c2}/\partial T|_{0.9\rho_n}|\partial B_{c2}/\partial T|^{-1}_{0.5\rho_n} = 5-8.$$

This relation[1)] does not agree too badly with similar estimates (~ 6), obtained on the basis of measurements of $B_{c2}(T)$ on single crystals of $YBa_2Cu_3O_{6+\delta}$ (Ref. 20). If we use the relation $B_{c2}(T\to 0)\approx 0.7T_c|\partial B_{c2}/\partial T|$, which is valid, for example, for sulfides of molybdenum with lead, which have record values of $B_{c2}(T\to 0)$ among traditional superconductors,[21] then in this case we obtain for the compounds $RBa_2Cu_3O_{6.9}$ the values $B_{c2\perp}(T\to 0)=450$–600 T and $B_{c2\parallel}(T\to 0)=70$–100 T and for specimens with Bi and Tl (Fig. 2) $B_{c2\perp}(T\to 0)=400$–500 T and $B_{c2\parallel}(T\to 0)=50$–80 T. Estimates of the anisotropic values of the coherence length give for specimens of all three systems: $\xi_\parallel(0)=2.5$–3.5 Å and $\xi_\perp(0)=18$–24 Å. It should be noted that the values of $\xi_\parallel(0)$ are somewhat smaller than the distance between the Cu–O planes and are approximately equal to the mean distance between the current carriers in these systems at their concentration $n_n=2\times 10^{22}$ cm^{-3} (Ref. 22).

As has already been discussed earlier,[18] the linear increase in $\rho(T)$ with increasing T in specimens of the composition $RBa_2Cu_3O_{6.9}$ may be associated with the existence in their phonon spectrum of local modes of the Einstein type with characteristic energy ~ 500 K. However, in that case the question arises of the possible reasons for the departure of $\rho(T)$ from linearity at an appreciable distance from T_c.

In principle, the non-linearity in the $\rho(T)$ dependences discussed can be produced by:

fluctuation effects;[23–25]

impurity phases with higher T_c;

inhomogeneities in composition within the confines of a single phase;

the influence of twins, near which a local increase in T_c is possible.[26]

In traditional compounds with three-dimensional superconductivity (for example, A-15) the relative contribution of fluctuational carrier pairing to the conductivity even at a small distance (<5 K) from T_c is extremely small and usually does not exceed hundredths of one percent. However, it can grow strongly in high temperature superconductors, characterized by a small coherence length and small conductivity $\sigma_n=\rho_n^{-1}$, typical values of which for polycrystalline specimens lie in the range 200–2000 $(\Omega\,\text{cm})^{-1}$.

As calculations have shown,[23] the contribution of fluctuational pairing to the conductivity above T_c for two- and three-dimensional systems should be characterized by power dependences of the form:

$$\Delta\sigma_{2D}(T)=\frac{e^2}{16\hbar d}\left(\frac{T-T_c}{T_c}\right)^{-1}, \tag{1}$$

$$\Delta\sigma_{3D}(T)=\frac{e^2}{32\hbar\xi(0)}\left(\frac{T-T_c}{T_c}\right)^{-1/2}, \tag{2}$$

where d is a characteristic dimension of a two-dimensional system and $\xi(0)$ is the coherence length for $T\to 0$.

If the departure from linearity of the $\rho(T)$ dependences below 200 K (Fig. 1) is ascribed to some extra conductivity $\Delta\sigma(T)$, then it is easy in this case to derive its change with temperature. In Fig. 3 is shown the relative change of the extra conductivity $\Delta\sigma/\sigma_R$ obtained in this way as a function of the normalized difference $(T-T_c)/T_c$ for two specimens: $ErBa_2Cu_3O_{6.9}$ ($T_c=91.7$ K, $\Delta T_c=1.5$ K, $\sigma_R=5\times 10^2$ $(\Omega\,\text{cm})^{-1}$, $\rho_{293\,K}/\rho_n=2.06$) and $Tl_2Ba_2Ca_2Cu_3O_{10+\delta}$ ($T_c=116$ K, $\Delta T_c=10$ K, $\sigma_R=2.5\times 10^2$ $(\Omega\,\text{cm})^{-1}$, $\rho_{293\,K}/\rho_n=2.93$), where T_c corresponds to the level $0.5\rho_n$, and $\sigma_R=\rho_{293\,K}^{-1}$. Even though the specimens have fairly different ΔT_c, the dependences of $\Delta\sigma$ in the temperature range $(T-T_c)\leqslant 10$ K are well approximated by power laws with exponent $-\frac{1}{2}$ (straight lines 1 and 2), which can be taken as an indication of the three-dimensional character of the superconductivity in these systems near T_c. Similar results were obtained earlier for specimens of $YBa_2Cu_3O_{6+\delta}$. (Ref. 27) The values of the coherence length calculated from Eq. (2), equal to 14 and 28 Å for specimens with Tl and Er respectively, are in reasonable agreement with the values $\xi_\perp(0)=18$–24 Å estimated from $B_{c2\parallel}(T\to 0)$ for a direction along the Cu–O layers, where the conductivity is a maximum. However, it should be noted that the values of $\xi(0)$ calculated from Eq. (2) for polycrystalline specimens can be raised severalfold by percolation effects, in that $\sigma<\sigma_\perp$ and $\Delta\sigma<\Delta\sigma_\perp$.

It can be seen from Fig. 3 that for both specimens at $T>1.1\,T_c$ a greater curvature is observed in the decrease of $\Delta\sigma$ compared with theory.[23] The following may be the reasons for such a divergence.

Firstly, Eqs. (1) and (2) were obtained on the basis of the Ginzburg–Landau theory which, strictly speaking, is applicable only near T_c. Far from T_c the dominant contribution to $\Delta\sigma(T)$ in compounds with small $\xi(0)$ must come from short-wavelength fluctuations, for the description of which serious difficulties arise in the GL theory. Attempts[28] to modify the theory[23] by artificially cutting off the contributin of short-wavelength fluctuatonal pairing far from T_c, nevertheless does not lead to satisfactory agreement with experimental results for $T>1.2\,T_c$.

Secondly, in the compounds considered, characterized by a quasilayer structure, the increase in the slope of the $\Delta\sigma$ dependences for $T>1.2\,T_c$ could be associated with a change in the dimensionality of the system ($3D$–$2D$ crossover). As has been shown recently,[29] the general expression

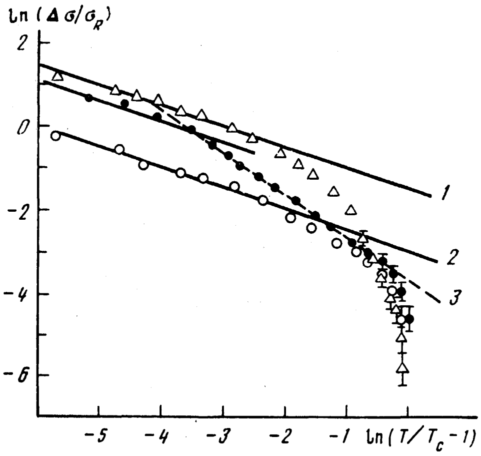

FIG. 3. The change in the normalized excess conductivity $\Delta\sigma/\sigma_R$ as a function of the relative temperature $(T-T_c)/T_c$ for specimens $Tl_2Ba_2Ca_2Cu_3O_{10+\delta}$ (△) and $ErBa_2Cu_3O_{6.9}$ (○,●) in the absence of a field (○) and in a field of 12 T (●). The straight lines 1 and 2 correspond to a power law $\Delta\sigma\propto(T-T_c)^{-1/2}$, the dashed line to the relation $\Delta\sigma\propto(T-T_c)^{-1}$.

for the fluctuational paraconductivity $\Delta\sigma_{LS}(T,B)$ of layered superconductors in a magnetic field B, can be written in the form

$$\Delta\sigma_{LS}(T, B)=\Delta\sigma_{AL}(T, B)+\Delta\sigma_{MT}(T, B), \quad (3)$$

where

$$\Delta\sigma_{AL}(T,B)=\frac{e^2}{16\hbar d_L\tau}\left[\frac{1}{(1+2\alpha)^{1/2}}-\frac{2+4\alpha+3\alpha^2}{4(1+2\alpha)^{5/2}}\frac{b^2}{\tau^2}+\ldots\right] \quad (4)$$

is the Aslamazov–Larkin fluctuational paraconductivity;

$$\Delta\sigma_{MT}(T,B)=\frac{e^2}{8\hbar d_L(1-\alpha/\delta)\tau}\left\{\ln\left[\frac{\delta}{\alpha}\frac{1+\alpha+(1+2\alpha)^{1/2}}{1+\delta+(1+2\delta)^{1/2}}\right]\right.$$
$$\left.-\left[\frac{\delta^2}{\alpha^2}\frac{1+\delta}{(1+2\delta)^{3/2}}-\frac{1+\alpha}{(1+2\alpha)^{3/2}}\right]\frac{b^2}{6\tau^2}+\ldots\right\} \quad (5)$$

is the Maki–Thompson paraconductivity, due to the interaction of unpaired current carriers with fluctuational Cooper pairs[24,25]

$$\alpha=2\xi_{\parallel}^2(0)/d_L^2\tau;\quad b=\frac{2e\xi_{\perp}^2(0)}{\hbar}B;$$

$$\tau=\frac{T-T_c}{T_c};\quad \delta=\frac{16}{\pi}\frac{\xi_{\parallel}^2(0)}{d_L^2}\frac{k_B\tau_\varphi}{\hbar};$$

τ_φ is the characteristic time for destruction of the phase of the order parameter, k_B is Boltzmann's constant, $\xi_{\parallel}(0)$ and $\xi_{\perp}(0)$ are the values of the coherence length for directions parallel and perpendicular to the c axis, and d_L is the distance between the layers.

Analysis of Eqs. (4) and (5) shows that over the whole temperature range from 1.005 T_c to 1.5 T_c (for $\tau < 5\times10^{-3}$ the theory of Ref. 29 is inapplicable due to the divergence of the expressions for $\Delta\sigma$) $\Delta\sigma_{MT}(T,B=0)$ changes appreciably more slowly with temperature than $\Delta\sigma_{AL}(T,B=0)$.

Since the experimental results for $T<1.15\ T_c$ are well described by Eq. (4), which in this temperature region is practically equivalent to Eq. (2), it can be concluded that near T_c the interaction of unpaired carriers with Cooper pairs should not have an appreciable influence on $\Delta\sigma_{LS}(T,B=0)$ in the present systems. A similar situation is also typical of traditional systems.[30]

On the other hand, estimates of the relative contribution of $\Delta\sigma_{AL}(T,B=0)$ and $\Delta\sigma_{MT}(T,B=0)$ from Eqs. (4) and (5) show that if, for example, for a specimen with Er one puts $\xi_{\parallel}(0)=3$ Å, $d_L=12$ Å, $\tau_\varphi\approx\hbar/\Delta(0)$ $\hbar/2k_BT_c$, then for $\tau=10^{-2}$, 5×10^{-2}, and 10^{-1} we obtain $\Delta\sigma_{AL}(T,B=0)/\Delta\sigma_{MT}(T,B=0)=3.5$, 1.6, and 1.3, respectively. It is possible that such a divergence is an indication of the appreciable role of scattering mechanisms for Cooper pairs in the systems studied, leading to their breakup and, correspondingly to lowering T_c compared with T_{c0} of an idealized system. As follows from an estimate,[31] $T_{c0}\approx2T_c$ and, consequently, $\Delta_{00}\approx2k_BT_{c0}$ $\approx4k_BT_c$. On substituting this value of Δ_{00} into Eq. (5) the ratio $\Delta\sigma_{AL}(T,B=0)/\Delta\sigma_{MT}(T,B=0)$ is roughly doubled, which can be fully reconciled with the experimental results.

Approximating the experimental values of $\Delta\sigma(T,B=0)$ by two straight lines corresonding to exponents $-\frac{1}{2}$ and -1, gives points of intersection at $\tau=0.13$ and 0.2 for specimens with Tl and Er, respectively. According to Hikami and Larkin[29] the critical value of τ_{cD} at which the 3D–2D crossover occurs is determined by the relation

$$\tau_{cD}=4[\xi_{\parallel}(0)/d_L]^2. \quad (6)$$

Substituting the values $d_L\approx c\approx12$ Å and $\tau_{cD}\approx0.2$ into Eq. (6) for a specimen with Er and $d_L\approx c/2\approx18$ Å and $\tau_{cD}\approx0.13$ for a specimen with Tl, we obtain $\xi_{\parallel}(0)=2.7$ Å and 3.3 Å, which agree well with estimates of $\xi_{\parallel}(0)=2.5$–3.5 Å obtained from the analysis of results of measuring $B_{c2}(T)$. In determining d_L for the $Tl_2Ba_2Ca_2Cu_3O_{10+\delta}$ specimen it was borne in mind that its elementary cell consists of two identical subcells (each with three C–O layers), shifted relative to one another by half the length of the transitional vector in the [110] direction.

It can be seen from Fig. 1 that a fairly high magnetic field $B=12$ T has practically no effect on the behavior of $\rho(T)$ for $T>1.15\ T_c$ (at least within the limits of 0.5%). This result agrees with precise measurements of magnetoresistance above T_c for $YBa_2Cu_3O_{6+\delta}$ specimens.[31] The influence of a magnetic field is, essentially, in accord with the broadening of the transition and its downward shift along the temperature scale. The dark circles in Fig. 3 show the change in $\Delta\sigma(T,B=12\text{ T})$ determined from the departure from a linear extrapolation for a specimen with Er as a function of the difference T/T_c-1, where T_c corresponds to the level $0.5\rho_n$ on the $\rho(T,B=12\text{ T})$ curve. The values of $\Delta\sigma(T,B=12\text{ T})$ obtained in this way in the range 1.05 T_c to 1.5 T_c are well approximated by a dependence of the form of Eq. (1), corresponding to the three dimensional case. Comparison of the $\Delta\sigma(T,B=0)$ and $\Delta\sigma(T,B=12\text{ T})$ dependences shows that under the action of a magnetic field an appreciable reduction of the temperature region takes place in which the behavior of the paraconductivity corresponds to the three-dimensional case. This is evidently associated with the fact that a magnetic field reduces the interaction between the layers, and as a result, leads to the suppression of long-wavelength fluctuations which make the major contribution to the paraconductivity near T_c. In principle, the influence of a magnetic field on $\Delta\sigma$ could be analyzed in more detail on the basis of Eqs. (4) and (5), but in this case more precise results obtained with single crystals are essential.

It follows from what has been said above that the departure from linearity of the $\rho(T)$ dependence for $T<1.5\ T_c$ in polycrystalline specimens can be satisfactorily explained within the framework of the theory of fluctuational superconductivity for layer systems.[29] However, the present state of the theory does not provide a unique answer to the question of the reasons for a strong reduction in the paraconductivity at $T>1.5\ T_c$, which has been noted by other authors.[27,32] It is evidently essential to consider the possibility of an additive contribution to $\Delta\sigma$ with a sharp fall-off for $T>1.5\ T_c$, as relevant to the present systems, for example from impurity phases with a critical temperature T_{ci} higher than that of the basic phase. Evidence of the existence of such phases comes, in particular, from singularities in the temperature dependences of the electrical resistance $R(T)$ for $T<160$ K observed on some specimens of the bismuth and thallium systems.[11,33]

One such dependence is shown in Fig. 4 for a specimen with stoichiometric composition $TlBaCa_3Cu_3O_{8+\delta}$. It can be seen that the step at 123 K agrees to within 1 K with the superconducting transition (curve 2) of a specimen consisting mainly of the phase $TlBa_2Ca_2Cu_3O_{8+\delta}$ with cell parameters $a = 3.847$ Å and $c = 15.88$ Å. It can be assumed that the peculiarities at 134 and 160 K are associated with superconducting transitions of phases with a more complicated structure. X-ray results, in particular, indicate that they are present in non-single-phase specimens. For example, in the Tl–Ba–Ca–Cu–O system a phase is found with cell parameters $a = 3.80$ Å and $c = 43.2$ Å, the conjectural composition of which corresponds to the formula $Tl_2Ba_2Ca_3Cu_4O_{12+\delta}$.

It is possible that phases with still more complicated structure (and a large number of Cu–O layers per cell) occur in specimens in such negligible amounts ($<2\%$) that they cannot be observed by x-ray methods. As has been shown by analysis of diffraction pictures of specimens of different phase composition, complication of the structure of perovskite-like phases, due mainly to an increase in the number of neighboring Cu–O layers, is accompanied by a growth in the number of Tl or Bi vacancies in the Tl–O or Bi–O layers dividing them, which must lead to a reduction in the probability of their formation, which means also in their relative concentration in multiphase specimens.

The question of a possible influence of inhomogeneity and twinning on the behavior of $\Delta\sigma(T)$ in the systems considered is, at present, very unclear. It can only be suggested that such an influence should be most appreciable near T_c.

Since thermodynamic fluctuations and impurity phases with higher values of T_c than the main phases should lead to an excess diamagnetism it would be interesting to bear this in mind when studying the magnetic properties of perovskite-like systems.

4. MAGNETIC PROPERTIES

Measurements of the magnetic characteristics of the specimens were carried out on a Kahn balance (in fields up to 0.43 T), on vibration and string magnetometers (in fields up to 14 T), and with the help of a sensitive fluxmeter in pulsed fields up to 45 T. Curves of the magnetic moment $M(B)$ at 4.2 K are shown in Fig. 5 for specimens of $YBa_2Cu_3O_{6.9}$, $Bi_2Sr_2CaCu_2O_{8+\delta}$ and $Tl_2Ba_2Ca_2Cu_3O_{10+\delta}$ (curves 1, 2 and 3 respectively), measured with a vibration magnetometer. An increase in the rate of sweeping the field led in a number of cases to the appearance of teeth on the $M(B)$ curves, similar to those usually found for jumps of magnetic flux.[34,35] It follows from the results obtained that for the most homogeneous specimens of $RBa_2Cu_3O_{6.9}$ the absolute values $|M(B)|$ at low temperatures ($T \ll T_c$) and low fields ($B < 1$ T) are 2–4 times larger than for specimens with Bi and Tl. It is by about this amount that the values of the frozen-in moment M ($B = 0$) on turning off the external field B, also differ. The $M(B)$ curves for $T < T_c$ for specimens of all three systems have the form characteristic for type II superconductors with large Ginzburg–Landau parameters $\varkappa = 50$–200 and with appreciable hysteresis, at any rate up to fields of 25–30 T. Measurements in pulsed fields for $B > 30$ T were complicated because of flux jumps and a sharp reduction in the signal/noise ratio.

If it is assumed that the superconducting transport current density J_c in the specimens is many times less than the critical current density J_{ci} in individual crystals, the mean dimensions of which are usually ~ 10 μm, then we obtain from the $M(B)$ curves at 4.2 K an order of magnitude for $J_{ci} = 10^5$–10^6 A/cm^2, which agrees with estimates of $J_{c\perp}$ for single crystals.[20] The steeper fall in $J_{ci}(B)$ for $B < 5$ T in specimens of the bismuth and thallium systems can be regarded as evidence of their smaller homogeneity compared with $RBa_2Cu_3O_{6.9}$.[34]

Investigation of flux creep was carried out both on a Kahn balance and with a sensitive magnetic field probe. In the first case the field was raised to its maximum value at fixed temperature, after which it was lowered smoothly (to prevent flux jumps) to the required value and held at a stable level for the whole time of the measurements. It can be seen from Fig. 6 that except for the initial section ($t < 200$ s), the reduced moment $M(t)/M(1)$ for specimens of all three systems decreased with time as $\log t$. The deviation of $M(t)$ from a logarithmic law for $t < 200$ s is evidently associated

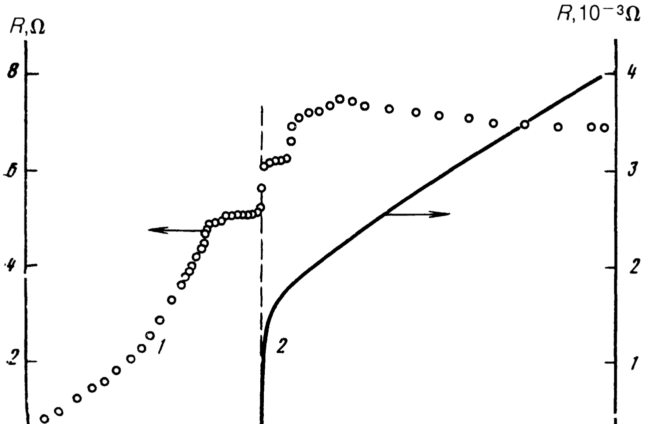

FIG. 4. Temperature dependences of the electrical resistance of specimens 1) $TlBaCa_3Cu_3O_{8+\delta}$ and 2) $TlBa2Ca_2Cu_3O_{8+\delta}$.

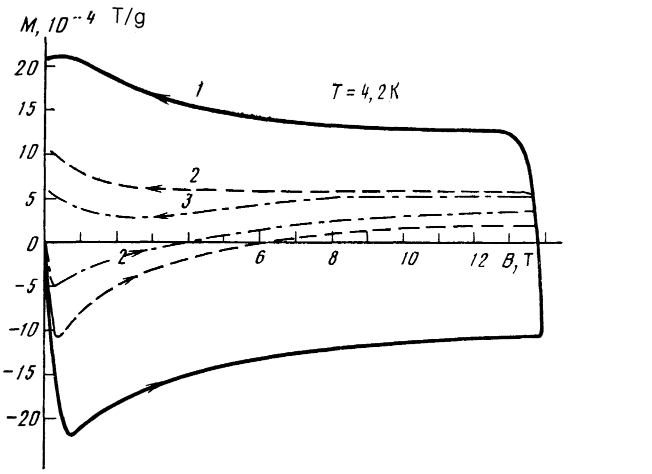

FIG. 5. The change of magnetic moment $M(B)$ with field B for specimens 1) $YBa_2Cu_3O_{6.9}$, 2) $Bi_2Sr_2CaCu_2O_{8+\delta}$, and 3) $Tl_2Ba_2Ca_2Cu_3O_{10+\delta}$ at $T = 4.2$ K.

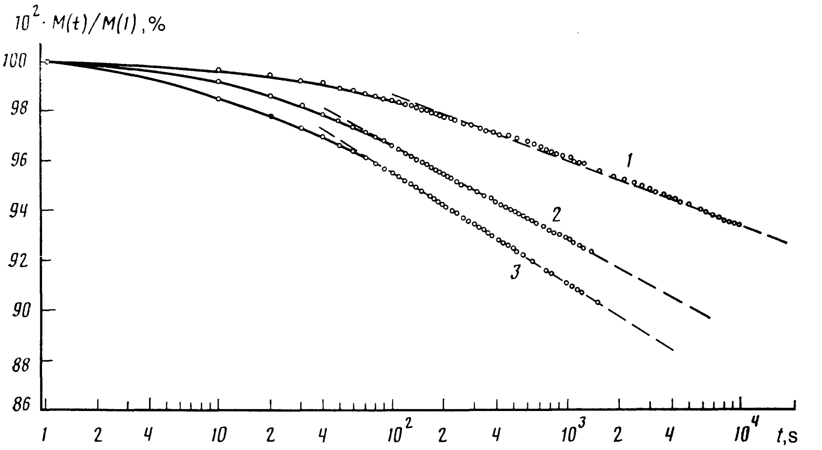

FIG. 6. The change in the reduced magnetic moment with time for specimens 1) $YBa_2Cu_3O_{6.9}$, 2) $Bi_2Sr_2CaCu_2O_{8+\delta}$, and 3) $Tl_2Ba_2Ca_2Cu_3O_{10+\delta}$ at 4.2 K and $B = 2.14\times10^{-2}$ T.

with relatively slow relaxation processes which bring the superconducting system (mainly the vortex lattice) into the thermodynamic equilibrium critical state[36] after fixing the external magnetic field. It should be noted that in the case of the molybednum chalcogenides[34,37] the $M(t)$ dependences becomes logarithmic after an appreciably shorter time interval ($\sim$20 s). A study of flux creep using magnetic probes, when the external magnetic field was completely removed ($B\to0$), did not reveal any appreciable differences in the behavior of $M(t)$ compared with the similar dependences, found in a field $B = 21.4$ mT (Fig. 6). On the basis of the $M(B)$ and $M(t)$ dependences obtained, the mean distance between the pinning centers and the effective inertial mass of a vortex can be estimated, in a similar way to that used by Alekseevskiĭ *et al.*[34] and by Mitin,[37] with the difference, however, that for quasilayered superconductors it is necessary to take account of the anisotropy in the effective masses of the current carriers and of the correlation length ($m_\parallel^*/m_\perp^* \propto \xi_\perp^2/\xi_\parallel^2$).

The temperature dependence of the magnetic susceptibility $\chi(t)$ for one of the specimens of the bismuth system, obtained in a field of 0.428 T is shown in Fig. 7a. The value of T_c determined at the $0.5\rho_n$ level in the given field is shown by the dashed line. The dash-dot line corresponds to a straight line in χ^{-1} and T coordinates. The change in character of the $\chi^{-1}(T)$ and $\chi(T)$ dependences for $T < 150$ K can be interpreted as a manifestation of additional diamagnetism $\Delta\chi(T)$. As in the case of the excess conductivity $\Delta\sigma(T)$, the change in the reduced excess diamagnetism $|\Delta\chi/\chi_R|$, if $\Delta\chi$ is defined as the difference between the values of $\chi(T)$ at $T < 160$ K and the extrapolation of the $\chi(T)$ dependence from high temperatures (dashed line), is well described near T_c (Fig. 7b) by a step function of the difference $(T - T_c)$ with an exponent $\alpha = -1/2$ (χ_R is the value of the magnetic susceptibility at $T = 293$ K). Such a dependence is close to that which is given by calculations of $\Delta\chi_\parallel(T)$ for quasilayered superconductors near T_c (Ref. 38) for a field orientation perpendicular to the layers, i.e., **B** parallel to the *c* axis:

$$\Delta\chi_\parallel(T) = -\frac{\pi k_B T}{6\Phi_0^2}\,\xi_\perp(0)\left(\frac{m_\parallel^*}{m_\perp^*}\right)^{1/2}\left[\tau + \frac{d_L^2\tau}{4\xi_\parallel^2(T)}\right]^{-1/2}, \qquad (7)$$

where $\Phi_0 = hc/2e$ is the flux quantum. Substituting into Eq. (7) $T = 89.5$ K, $\tau = 0.05$, $\xi_\perp(0) = 24$ Å, $\xi_\parallel(0) = \xi_\parallel(T)\tau^{1/2} = 3$ Å, $(m_\parallel^*/m_\perp^*)^{1/2} = \xi_\perp(0)/\xi_\parallel(0) = 8$. $d_L = c/2 \approx 15$ Å, we obtain: $\Delta\chi_\parallel(T) = -1.2\cdot10^{-6}$ cm³/g, which is 1.7 times smaller in absolute value than the experimental $\Delta\chi(T)$ at the same temperature. If we take it into account that the measurements were carried out on polycrystals, while $|\Delta\chi_\perp(T)| \ll |\Delta\chi_\parallel(T)|$ (Ref. 38), then this deviation should be even greater.

The departure of $\Delta\chi(T)$ from (7) starts roughly at the same values of τ_c as the cross-over on the $\Delta\sigma$ (T; $B = 0.5$ T) dependence for the given specimen. The great drop in $|\Delta\chi|$ at $T > 1.4T_c$ can be explained, as was done in the analysis of the

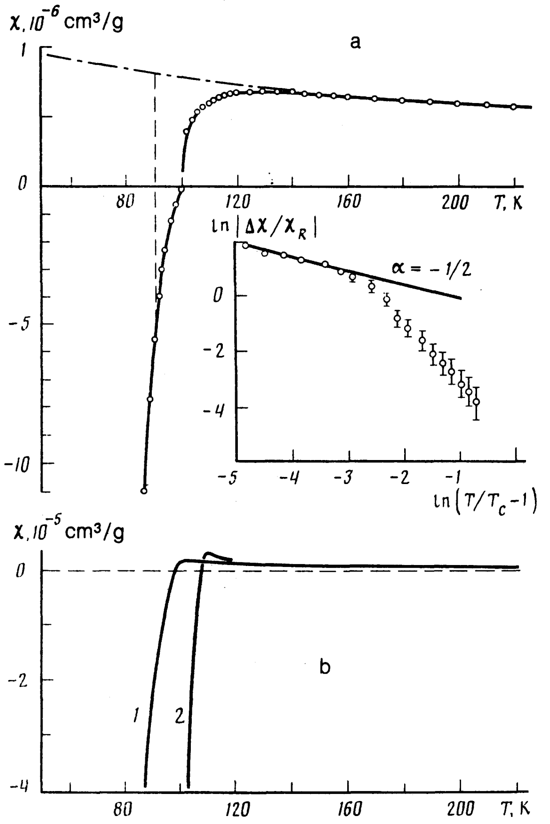

FIG. 7. a) Temperature dependences of the magnetic susceptibility $\chi(T)$ and of the normalized excess diamagnetism $|\Delta\chi/\chi_R|$, measured in a field $B = 0.428$ T for a specimen of $Bi_2Sr_2CaCu_2O_{8+\delta}$; b) the $\chi(T)$ dependence for a specimen of $YBa_2Cu_3O_{6.9}$ for two values of magnetic field: $B = 0.428$ and 0.0428 T (curves 1 and 2, respectively).

$\Delta\sigma(T)$ dependence, by the presence of an additive contribution from impurity phases. The existence of such a contribution is evidently also a reason for raising the values of the excess diamagnetism $\Delta\chi(T)$ compared with the estimates of $\Delta\chi_{\parallel}(T)$ from Eq. (7).

Specimens of the $RBa_2Cu_3O_{6+\delta}$ system have, in general, more curved $\chi(T)$ dependences near T_c than specimens of five-component systems. Figure 7b shows $\chi(T)$ dependences for a specimen of $YBa_2Cu_3O_{6.9}$, measured with a Kahn balance for two values of magnetic field $B = 428$ mT and 42.8 mT (curves 1 and 2 respectively). It is noteworthy that with a reduction in the applied field the diamagnetism of a specimen is preserved to an appreciably higher temperature, exceeding T_c (determined at the 0.5 ρ_n level) by almost 10 K. Such a strong influence of the magnetic field on the diamagnetic response of a specimen, bearing in mind the large values of $|\partial B_{c2}/\partial T|$, is rather unexpected and can hardly be explained just by fluctuational superconductivity,[23,39] for example, especially if we take into account the practically complete absence of the influence of a magnetic field $B = 12$ T on the non-linear section of $\rho(T)$ above T_c, which was used to establish $\Delta\sigma(T)$. The most plausible explanation must evidently be based on the assumption of the existence in the specimen of superconducting loops with Josephson-type weak links. Such loops could, for example, be formed by impurities of superconducting phases with higher T_c.

The shift upwards in temperature of the diamagnetic response on reducing B is also observed in specimens with Bi and Tl. However, the magnitude of this shift is in general appreciably less and amounts to only 2–4 K, which is possibly associated with their smaller uniformity, when even a small field of 0.43 T can almost completely destroy the superconducting currents in impurity phase loops, and correspondingly weaken the diamagnetic response. A similar situation is, for example, a characteristic of the transport current dependences $J_c(B)$ for polycrystalline specimens, when the contact between the crystallites is relatively weak (Josephson type). A sharper fall in $J_c(B)$ is observed in less uniform specimens with smaller values of $J_c(B\to 0)$ (Fig. 8).

5. CURRENT-VOLTAGE CHARACTERISTICS

Studies of the current–voltage characteristics (CVC) of tunneling junctions of the superconducting–normal metal type for perovskite-like superconducting ($T_c > 35$ K) phases of various compositions were carried out in the temperature range from 4.2 to 200 K. If the differential resistance dU/dI of such junctions is sufficiently high ($> 30\ \Omega$), an increase in the derivative dI/dU is observed in the $I(U)$ dependences in the range from 8 to 30 mV, while the CVC themselves are similar for all the specimens studied. The nonlinearity of the CVC is manifested more clearly if the ohmic constituent is calculated from the dependences obtained.

The CVC constructed in this way for one of the specimens of composition $Tl_2Ba_2CaCu_2O_{8+\delta}$ are shown in Fig. 9 at three values of the temperature: $T = 4.2$ K, 31 K and 120 K. Unlike the CVC of specimens with the K_2NiF_4 and 1–2–3 structures, studied earlier,[18] the dependences (for $T < J_c$) are shown in Fig. 9, the singularities for $U < 3$ mV, which could be produced by superconducting short circuits and have practically disappeared in a field of 8 T, are absent. Estimates of the superconducting energy gap Δ from the CVC obtained for $T \ll T_c$ show that for all the perovskite-like phases investigated the relation $2\Delta/k_B T_c = 3.5$–4.5 holds.

The magnitude of the energy gap Δ determined from the CVC in sufficiently uniform and single-phase specimens is practically independent of the location of the junctions. In less uniform specimens of the Tl–Ba–Ca–Cu–O system a change is observed not only in Δ but also in the local values of the critical temperature, which can be judged from the temperature dependence of the CVC. Vanishing of non-linearity on the CVC in the range $U < 5$ mV can then occur both below and above T_c (T_c corresponds to the 0.5 ρ_n level). Certainly, in the latter case the departure from linearity is usually so small even at $T = 1.2\ T_c$ that it approaches the noise level.

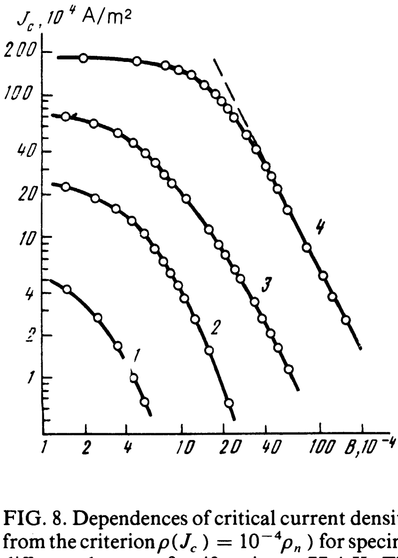

FIG. 8. Dependences of critical current density J_c on field B (determined from the criterion $\rho(J_c) = 10^{-4}\rho_n$) for specimens of $YBa_2Cu_3O_{6+\delta}$ with different degrees of uniformity at 77.4 K. The degree of uniformity increases with the number against each curve.

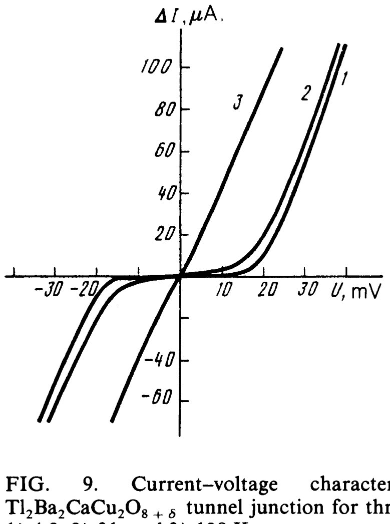

FIG. 9. Current–voltage characteristics of a tungsten–$Tl_2Ba_2CaCu_2O_{8+\delta}$ tunnel junction for three values of the temperature 1) 4.2, 2) 31, and 3) 120 K.

6. DISCUSSION OF THE RESULTS AND CONCLUSIONS

It follows from the results obtained that in contrast with specimens of the composition $RBa_2Cu_3O_{6+\delta}$, practically single-phase specimens of the five-component systems Tl–Ba–Ca–Cu–O and Bi–Sr–Ca–Cu–O are in general characterized by smaller uniformity. This is evidently associated with the fact that when the number of system components increases and the structure becomes more complicated the probability of onset of defects, and in particular of a disruption of the sequence of the layers, increases. Although from a crystallochemical point of view both five-component systems can be considered as analogous, one should expect that because of the smaller difference in the ionic radii of Ca and Sr the probability of breaking the layer sequence in a system with Bi would be higher. This is evidently one of the main reasons which hinder the obtaining of sufficiently single-phase specimens of the composition $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$.

It is interesting that partial substitution of Pb for Bi (or Pb + Sb) with subsequent long (≈ 60 h) annealing[40] enables the content of the given phase in the specimens to be increased appreciably. In the thallium system, such problems do not arise in obtaining specimens with a content of more than 80% of the phase $Tl_2Ba_2Ca_2Cu_3O_{10+\delta}$ ($c = 35.6$ Å, $T_c = 120$–130 K). In this system, varying the composition and of the synthesis temperature allows a minimum of three high-temperture ($T_c > 100$ K) superconducting phases to be obtained with parameters $c = 15.88$ Å, 19.23 Å and 29.5 Å. All these phases of the thallium system have very close values of the parameter $a = 3.83$–3.85 Å. Apart from this, in the non-single-phase specimens of this system there are found phases with the parameters $c = 39.5$ Å (Ref. 33) and 43.2 Å (Ref. 11) which, as has been suggested[11,33] have $T_c = 120$–150 K.

There is a tendency for an increase in T_c with increase of the parameter c, but it is, however, premature to talk about a clear-cut dependence of T_c on c on the basis of the existing data.

If the crystallographic data are analyzed, it can be noticed that within each class of compound a growth in T_c is accompanied by a reduction in the normalized mean distance between the layers $\bar{\varepsilon} = 2c/aq$, where c and a are the cell parameters and q is the number of layers in the cell.[11] Thus, for example, in the Bi–Sr–Ca–Cu–O system as $\bar{\varepsilon}$ decreases from 1.3 to 1.08 the value of T_c increases from 4–6 to 90–100 K. In this system, at smaller values of $\bar{\varepsilon}$ the phases are apparently structurally unstable under normal conditions. It is possible to dope them, for example, to increase their structural stability. In this way it is possible to reach $T_c = 132$ K in specimens of composition $(Bi_{1.6}Pb_{0.3}Sb_{0.1})Sr_2Ca_2Cu_3O_{10+\delta}$.[40] The dependence of T_c on $\bar{\varepsilon}$ extends to lower values of $\bar{\varepsilon}$ (at least down to $\bar{\varepsilon} = 1.02$) in the Tl–Ba–Ca–Cu–O system. If the $T_c(\bar{\varepsilon})$ dependences for the systems with Bi and Tl (Fig. 10) are extrapolated, then it appears that $T_c = 140$–150 K should correspond to values of $\bar{\varepsilon} = 0.95$. Raising T_c further in these systems seems unlikely, since under equilibrium conditions even doping is unlikely to achieve the necessary structural stability of phases for $\bar{\varepsilon} < 0.95$. It is not impossible, however, that such phases could appear under non-equilibrium conditions and take part in the form of inclusions in inhomogeneous and non-single-phase specimens, at the crystallite boundaries, for example. The existence of such inclusions, as has already been discussed above, could explain the steeper fall in the excess conductivity and excess diamagnetism with temperature, compared with the contribution from the thermodynamic fluctuations.

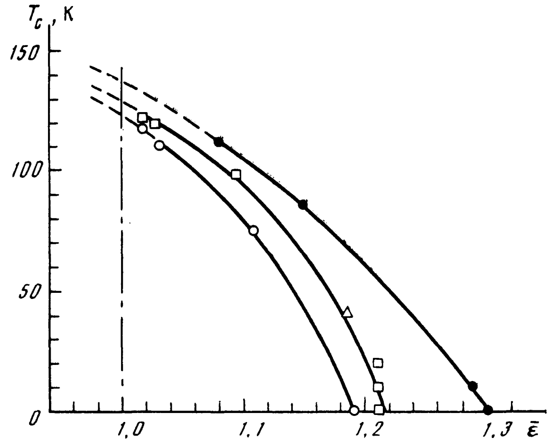

FIG. 10. Critical temperature as a function of the normalized mean distance $\bar{\varepsilon}$ between metal-containing layers in the phases: (○) $TlBa_2Ca_{n-1}Cu_nO_{2(n+1)+\delta}$, (□) $Tl_2Ba_2Ca_{n-1}Cu_nO_{2(n+2)+\delta}$, (●) $Bi_2Sr_2Ca_{n-1}Cu_nO_{2(n+2)+\delta}$, and (△) $La_{1.8}(Sr,Ba)_{0.2}CuO_{4-\delta}$.

The dependence of T_c on $\bar{\varepsilon}$ discussed above can be interpreted in the following way.

The data at present available show that the anisotropy in the physical properties of the perovskite-like phases with $T_c > 35$ K is due to the quasi-two-dimensional band formed mainly by the $2p_x + 2p_y$-oxygen orbitals and possibly the $3d_{x^2-y^2}$-Cu orbitals in the Cu–O layers, which are a general structural element for them. The position of the Fermi level E_F within this band (or around it) can change as a function of the oxygen content δ in a given phase. Thus, for example, in the most studied system $RBa_2Cu_3O_{6+\delta}$ the density of current carriers n_h as $\delta \to 0$ is close to zero and the band can be considered as practically full. An increase in δ leads to a downward shift in the energy E_F as a result of "suction" of part of the electrons out of the Cu–O layers introduced into the crystallographic lattice from oxygen atoms [which mainly fill the vacanices in the O(4) positions]. As a result, the density of states at the Fermi level $N(E_F)$, n_h and, consequently, the conductivity of the specimen increases. It is a characteristic that the temperature dependence of the electrical resistivity in the temperature range from 4.2 to 144 K for specimens with $\delta = 0.2$–0.3 is well described by an expression of the form:

$$\rho(T) = \rho_0 \exp\left(\frac{T}{T_0}\right)^{-1/(1+D)} \quad (8)$$

with the value $D = 2$ (Fig. 11). As is well known, such a $\rho(T)$ behavior corresponds to hopping conduction for a quasi-two-dimensional system with a small $N(E_F)$ and $dN(E_F)/dE \approx 0$. With a further increase in δ the $\rho(T)$ behavior is transformed from the two-dimensional ($D = 2$) to the three-dimensional ($D = 3$) case, which can be regarded as a strengthening of the interaction between the Cu–O layers. The reduction in the parameter c (mainly on account of

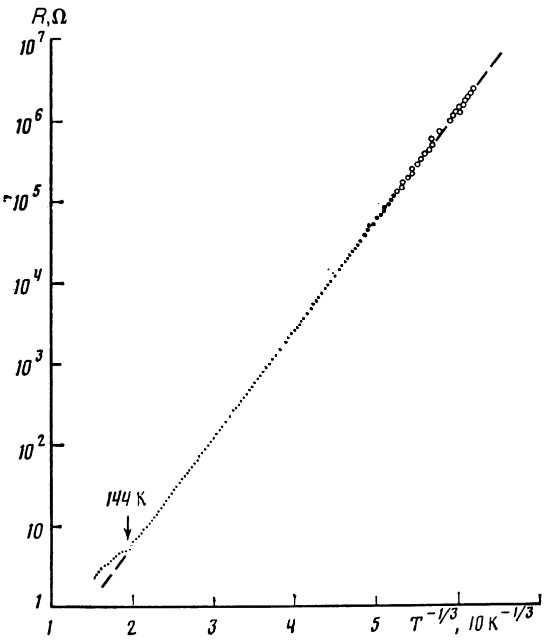

FIG. 11. Temperature dependence of the electrical resistance R of a specimen of $ErBa_2Cu_3O_{6+\delta}$ ($\delta \approx 0.2$).

the approach of the Cu–O and Ba–O layers) is also evidence of this.

At some threshold values $\delta_c \approx 0.4$, which depends, in particular, on the uniformity in the distribution of oxygen in the specimen, the hole density n_h in separate regions of it can be sufficient so that at low temperatures superconductivity arises there. Subsequent growth in n_h to $2\cdot 10^{22}$ (cm^{-3}) (Ref. 22) for $\delta \to 1$ is accompanied by the raising of T_c up to 93–95 K. It is possible that a further rise in n_h could lead to a reduction in T_c similar to that which occurs, for example, in the $La_{2-x}Sr_xCuO_4$ system.[41] It should also be remarked that the transition to the superconducting state in specimens of $YBa_2Cu_3O_{6+\delta}$ ($\delta = 0.85$–0.9) is accompanied by anomalous changes in the crystallographic parameter c,[42] while the parameters a and b do not then undergo noticeable changes.

In the less studied phases with Bi and Tl, reversible variations in the relative oxygen content also lead to changes in T_c over a fairly wide range. The question naturally arises: what factors determine the range of change in T_c?

The known superconducting perovskite-like phases can be divided into two groups. To the first group belong the phases in the crystallographic structure of which the Cu–O layers are separated by two or more metal-containing layers M–O ($M \neq Cu$), as, for example, in the systems: $La_{2-x}Sr_xCuO_{4+\delta}$, $BiSr_2CuO_{4+\delta}$, $TlBa_2CuO_{4+\delta}$, $Bi_2Sr_2CuO_{6-\delta}$ and $Tl_2Ba_2CuO_{6-\delta}$. For these phases the following condition is satisfied: $d\,|Cu_i\text{–}Cu_j| > d\,|Cu_i\text{–}Cu_i| \approx a$, where $d\,|Cu_i\text{–}Cu_j|$ and $d\,|Cu_i\text{–}Cu_i|$ correspond to the shortest distances between copper ions from separate layers and within each layer.

The distinguishing feature of phases of the second group is the existence in them of "packets" of n closely spaced Cu–O layers, between which there are single layers of the ions Ca, Sr, Ba, Y, R.

We shall first consider phases of the first group. It is reasonable to suppose that the interaction between the Cu–O layers will be reduced as the distance between them is increased, which in turn must be accompanied by a suppression of the quasi-two-dimensional bands and a corresponding growth in the density of states at the maximum of the $N(E)$ dependence. The position of the Fermi level within this band (or relative to it), as has already been noted above, depends mainly on the relative oxygen content in the given phase.

If we take it into account that in perovskite-like phases, as in traditional superconductors with strong binding, $T_c \propto N(E_F)\,\langle I_{ei}^2 \rangle$, where $\langle I_{ei}^2 \rangle$ is the square of the electron–phonon interaction matrix elements, averaged over the Fermi surface, then it can be concluded that the maximum values of T_c should be reached when the position of E_F is intermediate between the mobility limit and the maximum in $N(E)$ (where as a result of strong shielding the electron–ion interaction is drastically weakened and the system becomes a good metal). Within the framework of the approach presented it can additionally be concluded that

$$T_{c,\max} \propto \left| \frac{dN(E_F)}{dE} \right| .$$

In this way, among the known phases of the first group, we should expect the maximum values of T_c in the systems $Bi_2Sr_2CuO_{6-\delta}$ and $Tl_2Ba_2CuO_{6-\delta}$ with $d\,|Cu_i\text{–}Cu_j| \approx 12$ Å. This conclusion is confirmed both by the published data[43] and by our results, which show that $T_c = 85$–95 K can indeed be reached in $Tl_2Ba_2CuO_{6-\delta}$ specimens prepared under nonequilibrium conditions (quenched). It should be remarked that almost single-phase specimens ($a = 3.873$ Å, $c = 23.24$ Å) with such T_c are characterized by fairly high values of $\rho_{293\,K} \approx 10^{-2}$ (Ω cm and mildly sloping $\rho(T)$ dependences in the range from 100 to 300 K ($\rho_{293\,K}/\rho_n = 0.8$–1.2), which have a broad maximum at $T = 150$–200 K. Small reversible variations in oxygen content ($\Delta\delta \leqslant 0.04$) in specimens of $Tl_2Ba_2CuO_{6-\delta}$ lead to a much sharper change in T_c ($|dT_c/d\delta| \approx 10^3$ K) than is observed in, for example, the (La, Sr)$_2$ $CuO_{4-\delta}$ system[41] with $d\,|Cu_i\text{–}Cu_j| \approx 6.6$ Å. The 10–20 fold decrease of T_c for $Tl_2Ba_2CuO_{6-\delta}$ specimens with increase of the oxygen content, when the Fermi level is evidently shifted in the direction of the maximum in the $N(E)$ dependence, is accompanied by a reduction in $\rho_{293\,K}$ by tens of times, while the $\rho(T)$ dependence takes on the form characteristic for "good" metals with a ratio $\rho_{293\,K}/\rho_n = 20$–40, a record for perovskite superconducting phases.

On the whole, the existing data can be regarded as indirect confirmation of the model described above, in which the width of the quasi-two dimensional band depends on $d\,|Cu_i\text{–}Cu_j|$ and $T_{c,\max} \propto |dN(E_F)/dE|$.

On the other hand, the larger $d\,|Cu_i\text{–}Cu_j|$, the more probable are mechanisms for suppressing superconductivity, including, for example, the destruction of pairs in the interaction with normal electrons from neighboring layers, thermodynamic fluctuations, structural defects, etc. (The influence of all these unfavorable factors on the superconductivity can greatly weakened if the structure of the phases consists of blocks of several ($n \geqslant 2$) interacting layers with $d\,|Cu_i\text{–}Cu_j| \leqslant d\,|Cu_i\text{–}Cu_i|$, instead of single Cu–O layers.) Although this leads to a broadening of the quasi-two-dimensional band, it may on the whole be possible to hope to obtain an appreciable gain the raising of T_c. As model calculations show,[45,46] when n is increased in $M_2A'_2Ca_{n-1}Cu_nO_{2(n+2)+\delta}$ (M = Bi, Tl; A' = Sr, Ba) the value of T_c should grow monotonically and reach an asymptote with $T_{c,max}$ = 135–145 K. The calculated values of T_c for $n \leqslant 4$ will then agree well with the experimental results.[10,11,14]

Analysis of the crystallographaphic results[14,44,47] shows that the Cu–O layers are positioned closest to one another and the metal-containing layers are next to them. It follows that the larger the number of Cu–O layers in the elementary cell of a given phase, the smaller the mean normalized distance $\bar{\varepsilon} = 2c/aq$ between the layers, since the parameter a is practically unchanged thereby.[11,48]

The $T_c(\bar{\varepsilon})$ dependence shown in Fig. 10 thus mainly reflects the interconnection between: 1) the raising of T_c and the increase in n—the number of "narrow" Cu–O layers in the total number q of metal–containing layers in the elementary cell; 2) the reduction in the degree of populating of the Bi and Tl positions with an increase in n, which is also accompanied by a reduction in $\bar{\varepsilon}$. In addition, within the confines of each equilibrium phase with $n \geqslant 2$, reversible changes in the oxygen content can lead to a simultaneous change in T_c and c in such a way that a growth in T_c will be accompanied by a reduction in $\bar{\varepsilon}$.[49]

The raising of T_c in phases with $n \geqslant 2$ is accompanied by an increase in the relative oxygen content, which for large n only becomes possible at the expense of increasing the vacancies of Bi, Tl and possibly of other metals. In the initial stages of this process an increase in the number of vacancies can exert a stabilizing action on the phase structure, but when their concentration exceeds a limiting value one must expect just the opposite effect—a sharp reduction in the stability of the phases, for example for $\bar{\varepsilon} \leqslant 0.95$.

In spite of the technological difficulties in synthesizing sufficiently stable phases with complicated structures, the results provide a basis for concluding that in the quasi-layered perovskite-like systems superconductors can be obtained with $T_{c,max}$ = 150–160 K, and further studies are needed to make more precise their composition and the method of preparation.

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[1)]The use of the upper half of the resistive transition curves ($\rho \geqslant 0.5\rho_n$) is explained by the fact that in this case other (apart from anisotropy) reasons for a broadening of the superconducting transition have appreciably less influence, due, for example, to diffusion of vortices under weak pinning conditions.

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

[2]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).

[3]N. E. Alekseevskiĭ, E. P. Khlybov, G. M. Kuz'mivheva *et al.*, Proc. Conf. on Problems of High-Temperature Superconductivity [in Russian], Sverdlovsk (1987), Part 1, p. 88.

[4]Y. LePage, T. Siegrist, S. A. Sunshine, L. F. Schneemeyer, D. W. Murphy, S. M. Zahurak, J. V. Waszczak, W. R. McKinnon, J. M. Tarascon, G. W. Hull, and L. H. Greene, Phys. Rev. B **36**, 3617 (1987).

[5]C. Michel, M. Hervieu, M. M. Borel, A. Grandin, F. Deslandes, J. Provost, and B. Raveau, Z. Phys. B **68**, 421 (1987).

[6]M. Maeda, Y. Tanaka, M. Fukutomi, and T. Asano, Jpn. J. Appl. Phys. **27**, L209 (1988).

[7]R. M. Hazen, C. T. Prewitt, R. J. Angel, N. L. Ross, L. W. Finger, C. G. Hadidiacos, D. R. Veblen, P. J. Heaney, P. H. Hor, R. L. Meng, Y. Y. Sun, Y. Q. Wang, Y. Y. Xue, Z. J. Huang, L. Gao, J. Bechtold, and C. W. Chu, Phys. Rev. Lett. **60**, 1174 (1988).

[8]Z. Z. Sheng and A. M. Hermann, Nature (London) **332**, 138 (1988).

[9]R. M. Hazen, L. W. Finger, R. J. Angel, C. T. Prewitt, N. L. Ross, C. G. Hadidiacos, P. J. Heaney, D. R. Veblen, Z. Z. Sheng, A. Elali, and A. M. Hermann, Phys. Rev. Lett. **60** 1657 (1988).

[10]S. S. P. Parkin, V. Y. Lee, E. M. Engler, A. I. Nazzal, T. C. Huang, G. Gorman, R. Savoy, and R. Beyers, Phys. Rev. Lett. **60**, 2539 (1988).

[11]N. E. Alekseevskiĭ, G. M. Kuz'micheva, E. P. Khlybov, A. V. Mitin, and V. I. Nizhankovskiĭ, Pis'ma Zh. Eksp. Teor. Fiz. **48**, 45 (1988) [JETP Lett. **48**, 47 (1988)]; N. E. Alekseevskiĭ, A. V. Mitin, G. M. Kuz'micheva, V. V. Evdokimova *et al.* Sverkhprovodimost'; fizika, khimiya, technika [Superconductivity; Physics, Chemistry, Technology], 1989, Vol. 2, p. 81.

[12]A. Santoro, F. Beech, M. Marezio, and R. J. Cava, Physica (Utrecht) C **156**, 693 (1988).

[13]D. S. Ginley, E. L. Venturini, J. F. Kwak, R. J. Baughman, M. J. Carr, P. F. Hlava, J. E. Shirber, and B. Morosin, Physica (Utrecht) C **152**, 217 (1988).

[14]S. S. P. Parkin, V. Y. Lee, A. I. Nazzal, R. Savoy, R. Bereys, and S. J. LaPlaca, Phys. Rev. Lett. **61**, 750 (1988).

[15]R. S. Liu, P. T. Wu, J. M. Liang, and L. J. Chen, High T_c Update, **2**, No. 19, 1 (1988).

[16]N. E. Alekseevskiĭ, A. V. Mitin, V. I. Nizhankovskiĭ, B. Gren, and J. Warchulska, J. Less-Common Met. **147**, L21 (1989).

[17]M. Oussena, S. Sennoussi, G. Collin, J. M. Broto, H. Rakato, S. Askenazy, and J. C. Ousset, Phys. Rev. B **36**, 4014 (1987).

[18]N. E. Alekseevskiĭ, E. P. Khlybov, G. M. Kuz'micheva, V. V. Evdokimova, A. V. Mitin, V. K. Nizhankovskiĭ, and A. I. Kar'kovskiĭ, Zh. Eksp. Teor. Fiz. **94** (5), 281 (1988) [Sov. Phys. JETP **67**, (5) 1025 (1988)].

[19]N. E. Alekseevskiĭ, A. V. Mitin, V. N. Samosyuk, and V. I. Firsov, Zh. Eksp. Teor. Fiz. **85**, 1092 (1983) [Sov. Phys. JETP **58**, 635 (1983)].

[20]T. K. Worthington, W. J. Gallagher, D. L. Kaiser, F. H. Holtzberg, and T. R. Dinger, Physica (Utrecht) C **153**, 32 (1988).

[21]N. E. Alekseevskiĭ, A. V. Mitin, Ch. Bazan, N. M. Dobrovol'skiĭ, and R. Raczka, Zh. Eksp. Teor. Fiz. **74**, 384 (1978) [Sov. Phys. JETP **47**, 199 (1978)].

[22]G. S. Grader, P. K. Gallagher, and A. T. Fiory, Phys. Rev. B **38**, 844 (1988).

[23]L. G. Aslamazov and A. I. Larkin, Phys. Lett. A **26**, 238 (1968).

[24]K. Maki, Prog. Theor. Phys. **39**, 897 (1968); **40**, 193 (1968).

[25]R. S. Thompson, Phys. Rev. B **1**, 327 (1970).

[26]M. S. Khaĭkin and I. N. Khlyustikov, Pis'ma Zh. Eksp. Teor. Fiz. **33**, 167 (1981) [JETP Lett. **33**, 158 (1981)].

[27]P. P. Freitas, C. C. Tsuei, and T. S. Plaskett, Phys. Rev. B **36**, 833 (1987).

[28]W. L. Johnson and C. C. Tsuei, Phys. Rev. B **13**, 4827 (1976).

[29]S. Hikami and A. I. Larkin, Modern Phys. Lett. B **2**, 693 (1988).

[30]R. E. Glover, Phys. Lett. A **25**, 542 (1967).

[31]Y. Matsuda, T. Hirai, and S. Komiyama, Solid State Commun. **68**, 103 (1988).

[32]M. Carrera, X. Granados, J. Fontcuberta, M. Vallet, and J. M. González-Calbet, Physica (Utrecht) C **157**, 285 (1989).

[33]J. M. Laing, R. S. Liu, L. Chang, P. T. Wu, and L. J. Chen, Appl. Phys. Lett. **53**, 1434 (1988).

[34]N. E. Alekseevskiĭ, A. V. Mitin, and E. P. Khlebov, Zh. Eksp. Teor. Fiz. **82**, 927 (1982) [Sov. Phys. JETP **55**, 543 (1982)].

[35]M. Guillot, M. Potel, P. Gougeon, H. Noel, J. C. Levet, G. Chouteau, and J. L. Tholence, Phys. Lett. A **127**, 363 (1988).

[36]C. P. Bean, Phys. Rev. Lett. **8**, 250 (1962).

[37]A. V. Mitin, Zh. Eksp. Teor. Fiz. **93**, 590 (1987) [Sov. Phys. JETP **66**, 335 (1987)].

[38]H. Obara, K. Uchinokura, and S. Tanaka, Physica (Utrecht) C **157**, 37 (1989).

[39]A. Schmid, Phys. Rev. **180**, 527 (1969); R. E. Prange, Phys. Rev. B **1**, 2349 (1970).

[40]H. Liu, L. Gao, L. Zhou *et al.*, High T_c Update **2** No. 24, 1 (1988).

[41]J. B. Torrance, Y. Tokura, A. I. Nazzal, A. Bezinge, T. C. Huang, and S. S. P. Parkin, Phys. Rev. Lett. **61**, 1127 (1988).

[42]H. Srinivasan, K. S. Girirajan, V. Ganesan, V. Radhakrishnan, and G. V. Subba Rao, Phys. Rev. B **38**, 889 (1988).

[43]C. C. Torardi, M. A. Subramanian, J. C. Calabrese, J. Gopalakrishnan, E. M. McCarron, K. J. Morrissey, T. R. Askew, R. B. Flipper, U. Chowdhry, A. W. Sleight, P. Marsh, L. W. Rupp, and W. F. Peck, Phys. Rev. B **38**, 225 (1988).

[44]Y. Shimakawa, Y. Kubo, T. Manako, T. Satoh, S. Iijima, T. Ichihashi,

and H. Igarashi, Physica (Utrecht) C **157**, 279 (1989).
[45]J. M. Wheatley, T. G. Hsu, and P. W. Anderson, Nature (London) **333**, 121 (1988).
[46]C. H. Eab and I. M. Tang, Phys. Lett. A **134**, 253 (1989).
[47]S. A. Sunshine, T. Siegrist, L. F. Schneemeyer, D. W. Murphy, R. J. Cava, B. Batlogg, R. B. van Dover, R. M. Fleming, S. H. Glarum, and S. Nakahara, Phys. Rev. B **38**, 893 (1988).
[48]B. Morosin, D. S. Ginley, E. L. Venturini, P. F. Hlava, R. J. Baughman, J. F. Kwak, and J. E. Schirber, Physica (Utrecht) C **152**, 223 (1988).
[49]I. Iguchi and A. Sugushita, Physica C **152**, 228 (1988).

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