

High- T_c superconductors from the experimental point of view

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An analysis is made of experimental data from measurements of the specific heat, the resistivity, the critical magnetic fields, the paramagnetic susceptibility above T_c , the Hall effect, and of other properties of the two new types of superconducting materials: lanthanum cuprates and the 1-2-3 compounds. The results of this analysis are discussed from the point of view of applying the Fermi-liquid picture to the description of the normal and superconducting properties of these materials, the role of fluctuations near the critical temperature, and the dimensionality of the superconductivity in them. Estimates of the width of the conduction band and of some other microscopic parameters indicate that there is a rather wide (about 0.7 eV) delocalized band. The fluctuations region near T_c is narrow, but nonetheless wider than that in ordinary superconductors. The superconductivity near T_c is three-dimensional, although sufficiently far from T_c the layered nature of the structure may be important.

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1. INTRODUCTION

Since the discovery of high-temperature superconductivity¹ a great deal of experimental material has been accumulated regarding the superconducting and normal properties of the new compounds. However, a theoretical understanding of high-temperature superconductivity has still not been attained. Such an understanding has to a large extent been hindered by the disconnected nature of the experimental data and the large amount of scatter in it. Even the properties of the new materials in the normal phase have not been thoroughly studied.

In this paper we have attempted to make some generalizations and interpretations of the existing experimental data in order to throw light on the following fundamental questions: 1) how wide is the fluctuation region near T_c ?; 2) To what extent does the anisotropy of the properties of the new materials affect their superconducting properties?; 3) Is it possible to use the Fermi liquid picture to describe the normal and superconducting properties of these compounds (putting aside the specific pairing mechanism)?; In other words, can the properties of the new materials in the normal phase be described under the assumption that above T_c there is a rather wide delocalized electron band? All these questions arise naturally, first, because of the large volume of the unit cell and the pronounced layered nature of the crystal structure of the new superconductors, and, second, simply from the fact that these materials exhibit a high critical temperature. If we begin from the Fermi liquid picture, then the factors that we have enumerated above would imply, on the one hand, a low carrier concentration (and a small Fermi momentum) and a large quasiparticle effective mass (which is equivalent to a narrow conduction band). On the other hand, according to the usual ideas, the high values of T_c along with a large effective mass gives an extremely small

coherence length $\xi_0 = \hbar v_F / 2\pi T_c$. All of these considerations taken together point to values of T_c/E_F or $\hbar/p_F \xi_0$ that are not very favorable for the usual picture of superconductivity.

An alternative to the Fermi liquid approach is the idea of a strongly correlated electron system. Such ideas are attractive because by hypothesizing only a large characteristic interaction energy between the electrons and conditions under which the appropriate pairing mechanism operates, high values of T_c are easily possible, values which are perhaps even comparable in order of magnitude to the corresponding electron energy E_0 . An example of the application of these ideas is the so-called resonating valence bond model of Anderson.² In particular, an important qualitative conclusion that follows from this model is the existence of gapless fermions which carry no charge but have spin. In this way the model predicts that the specific heat at low temperatures, as well as in the superconducting state, must depend linearly on the temperature T . A linear term in the specific heat is indeed seen in most of the experiments at temperatures below T_c , but it is still hard to say whether it is a consequence of the intrinsic properties of the superconducting state or of the presence of impurities of nonsuperconducting phases. Some interesting results, which we discuss below in Section 5, have been obtained³ for the dependence of the linear term in the specific heat on the concentration of strontium in the compound $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$.

In order to make a choice between these points of view and, in particular, to check the correctness of the hypothesis of delocalized electrons, it is important to have an estimate of the ratio of T_c to the characteristic electron energy. The width of the fluctuation region near T_c would also be related to this ratio.

The question of "two-dimensional" superconductivity

TABLE I. Experimental data for ceramic and single crystal samples of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($x \geq 0.15$).

| T_c , K and Refs. | ρ , $\mu\Omega \cdot \text{cm}$ | $d\rho/dT$ $\mu\Omega \cdot \text{cm}/\text{K}$ | $-dH_{c2}/dT$, T/K | $-dH_{c1}/dT$, Oe/K | $\Delta C_p/T_c$, mJ/K^2 , (mole Cu) | χ_{Pauli} , $10^{-4} \text{cm}^3/$ (mole Cu) | ω_p , eV | n , 10^{21} cm^{-3} | θ_D , K |
|------------------------|---|--|--|-------------------------|---|--|--------------------------------------|-------------------------------------|----------------------|
| Ceramic | | | | | | | | | |
| 34 ⁵ | 430 (T_c) ⁵ | 6.8 ⁵ | 2.7 ⁵ | | 7.6 ⁹ | 1.6 ¹⁵ | 1.7 ⁶ | 6 ¹⁹ | 300 ²⁰ |
| 40 ⁷ | 300 (T_c) ⁷ | 6 ⁷ | 1.75 ⁹ | 5.1 ⁹ | 24 ¹³ | 1.4 ⁴¹ | $0.9\epsilon_0^{1/2b}$ ⁴¹ | 2.1 ^d ⁶⁶ | 400 ^{42,43} |
| 33 ^{10,48} | 320 (T_c) ⁹ | 4.4 ^{10,48} | 1.5 ^{10,48} | | 17 ¹⁵ | 1.6 ^{42,43} | $0.8\epsilon_0^{1/2b}$ | 3.7 ^d ⁶⁷ | 450 ¹⁶ |
| 36 ¹⁵ | 400 (T_c) ^{10,48} | 4.7 ³⁶ | 2.2-4.5 ¹¹ | | 20 ¹⁶ | 1.5 ⁵⁷ | | 2 ^d ⁶⁸ | |
| 31 ¹⁶ | 100 (res) ³⁶ | 4 ^a ⁵⁰ | 2.5 ³⁸ | | 10 ²⁰ | 1.6 ⁶¹ | | | |
| 37 ²⁰ | 350 (T_c) ⁴⁷ | 3.4 ^a ⁶⁵ | 1.7 ⁴⁵ | | 14 ^{42,43} | | | | |
| 33 ⁴⁵ | 300 (res) ⁶⁵ | | 1.3-4 ⁴⁷ | | | | | | |
| 34 ⁴⁷ | | | | | | | | | |
| Single crystal | | | | | | | | | |
| 30-33 ^{4,44} | $\rho_{ab}(T_c) = 10$ ³ $\rho_c/\rho_{ab} = 19$ ^{4,44} | 1.7 ⁸ | [0.3(H c) 4(K c)] ^{4,44} | | | | | 6-9 ^c ⁴⁰ | |
| 23 ⁸ | $\rho_{ab}(T_c) = 250$ ⁸ | | | | | | | 5-7 ^c ⁸ | |

^a Linear dependence maintained approximately to 1100 K.

^b The permittivity ϵ_0 due to the polarization of the ion cores was not determined. The value $\epsilon_0 = 4$ was used in Ref. 6.

^c The carrier concentration, defined as $n = (R_H ec)^{-1}$ increases with the temperature and varies in this interval as the temperature is increased from T_c to 300 K.

^d Depends on the strontium content (see Sec. 5).

arises because of the large anisotropy that is observed, both in measurements of the resistivity, and of the critical magnetic fields. There is no single point of view on this issue, either.

In order to provide an answer to the questions we have posed, we have attempted to analyze the existing published experimental data on the variation of the specific heat, the resistivity, the critical magnetic fields, the magnetic susceptibility above T_c , the Hall effect, and other measured quantities. Our review makes no claim to being exhaustive. The amount of experimental data could easily be expanded. Nonetheless, in summarizing these data we can say that most of the experimental data on the superconducting properties do not contradict the hypothesis that there is a rather wide delocalized band. The fluctuation region near T_c turns out to be rather narrow, and the superconductivity appears most likely to be three-dimensional. The two-dimensional character, or, more precisely, the layered structure, would

be an important factor in a quantitative description only at temperatures quite far from T_c .

2. EXPERIMENTAL DATA

The experimental data discussed below, coming from measurements of the specific heat, the critical magnetic fields, the paramagnetic susceptibility above T_c , and the Hall effect, are collected in Tables I-III. In these tables we include results obtained from the compounds $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ and $\text{YBa}_2\text{Cu}_3\text{O}_7$. In many cases the results depend on the composition. This last point merits a special discussion, which we will include at the end of this article (see Sec. 5). With regard to the experimental data as a whole, it should be said that they exhibit a considerable amount of scatter. It is not entirely clear whether this scatter is associated with the composition (mainly with poor control of the composition), or with shortcomings in sample quality, including the methods of preparation. A fundamental diffi-

TABLE II. Experimental data for $\text{YBa}_2\text{Cu}_3\text{O}_7$ ceramic samples.

| T_c , K | ρ , $\mu\Omega \cdot \text{cm}$ | $d\rho/dT$ $\mu\Omega \cdot \text{cm}/\text{K}$ | $-dH_{c2}/dT$, T/K | $-dH_{c1}/dT$ Oe/K | $-dH_{cm}/dT$, Oe/K | $\Delta C_p/T_c$, mJ/K^2 , (mole Cu) | χ_{Pauli} , $10^{-4} \text{cm}^3/$ (mole Cu) | ω_p , eV | n , 10^{21} cm^{-3} | θ_D , K |
|------------------|--------------------------------------|--|------------------------|-----------------------|--------------------------------|---|--|-------------------|-------------------------------------|----------------------|
| 92 ¹⁷ | 200-250(T_c) ¹⁷ | 1.7-2.5 ¹⁷ | 1.3 ¹⁷ | 7 ¹⁷ | $1.8 \cdot 10^2$ ⁵⁹ | 21 ¹² | 1.9 ²⁵ | 2.6 ²⁹ | > 4.2 ¹⁸ | 440 ³² |
| 92 ²⁷ | 250(res) ²⁶ | 0.8 ²⁶ | 1.9 ¹⁸ | 9 ³⁹ | | 13 ²⁶ | 1.3 ²⁶ | 2.1 ³⁴ | 3.5-10 ^b ²⁶ | 360 ³⁵ |
| 95 ²⁸ | 200(T_c) ²⁸ | 1.9 ²⁸ | 1.2-4.5 ²⁶ | 17 ⁶² | | 13 ²⁷ | 1.3 ²⁷ | | 10 ^c ³⁰ | 380 ^{42,43} |
| 93 ³¹ | 510(T_c) ³⁹ | 2 ^a ⁵⁰ | 4.6 ²⁷ | | | 15 ³² | 1.6 ³¹ | | < 3.1 ^d ⁶⁹ | 400 ⁶⁰ |
| 90 ³² | 200(T_c) ⁴⁷ | | 4.6 ³⁸ | | | 23 ³⁵ | 1.5 ³⁵ | | | |
| 90 ³⁷ | | | 1.25 ³⁹ | | | 13 ^{42,43} | 1.8 ³⁷ | | | |
| 92 ³⁹ | | | 2.3 ⁴⁵ | | | 11 ⁶⁰ | 1.3 ^{42,43} | | | |
| 90 ⁴⁵ | | | 2.2 ⁴⁶ | | | 23 ⁶² | 1.1 ⁷⁰ | | | |
| 95 ⁴⁷ | | | 2.2-3.6 ⁴⁷ | | | 19 ⁷⁰ | | | | |
| 93 ⁶² | | | 3 ⁵¹ | | | | | | | |
| 92 ⁶³ | | | 4.6 ⁵⁹ | | | | | | | |
| | | | 2 ⁶² | | | | | | | |
| | | | 3.2 ⁶³ | | | | | | | |

^a Linear dependence maintained up to about 550 K.

^b Carrier concentration, defined as $n = (R_H ec)^{-1}$ increases with temperature and varies in the indicated interval as the temperature is raised from 100 K to 300 K.

^c Calculated on the basis of magnetic measurements.

^d Depends on the oxygen content (see Section 5).

TABLE III. Experimental data for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystal samples.

| T_c K | ρ_{ab} $\mu\Omega \cdot \text{cm}/\text{K}$ | $d\rho_{ab}/dT$, $\mu\Omega \cdot \text{cm}/\text{K}$ | $\rho_c(T_c)/\rho_{ab}(T_c)$ | $-dH_c/dT$, T/K H c H⊥c | χ_{Pauli} 10^{-4} $\text{cm}^3/(\text{mole Cu})$ | ω_p , eV | n , 10^{21} cm^{-3} |
|-----------------------|---|---|------------------------------|------------------------------------|--|--------------------|------------------------------------|
| 90 ⁴⁴ | 200 (res) ²² | 6 ²² | 95 ⁵² | {0.37-0.9 ²¹ | 1.8 ¹⁴ | 2.6 ⁵³ | 7-9 ⁵² |
| 89 ⁴⁹ | 200 (res) ²³ | 6 ²³ | 230 ⁵⁶ | {1.1 ²³ | | | 3-6 ⁶⁴ |
| 90 ⁵³ | 135 (res) ²⁴ | 2 ²⁴ | | {3.8 ²³ | | | |
| 90 ⁵⁴ | 400 (res) ³³ | 2 ³³ | | {0.37-0.9 ²² | | | |
| 92 ⁵⁴ | 75 (res) ⁵² | 1.3 ⁵² | | {3 | | | |
| 93 ^{b 55} | 15 (res) ⁵³ | 1.2 ⁵³ | | {0.37 ⁴⁴ | | | |
| 60-80 ^{c 55} | 140 (T_c) ⁵⁴ | 1.5 ⁵⁴ | | {2 | | | |
| 90 ⁵⁶ | 54 (T_c) ^{b 55} | | {0.93 ⁶⁴ | {0.46 ⁴⁹ | | | |
| | 150 (T_c) ^{c 55} | 1.3 ^{c 55} | {2.3 | {2.3 | | | |
| | 60 (T_c) ⁵⁶ | 0.9 ⁵⁶ | | {0.2-1.1 ⁵⁴ | | | |
| | | | | {0.7-3.6 | | | |
| | | | | {0.96 ⁵⁴ | | | |
| | | | | {4.0 | | | |

^a Carrier concentration increases in the indicated interval as the temperature is raised from 100 K to 300 K.

^b Orthorhombic phase.

^c Tetragonal phase.

culty in the analysis of the data is that different characteristics have usually been measured for different samples in different laboratories. A unified study of various properties on the same sample is still a rarity.

In determining the Pauli susceptibility χ_{Pauli} from the measured paramagnetic susceptibility above T_c it is usual to introduce a correction for the diamagnetism of the ion cores using the values $\chi_{\text{core}} = -0.98 \cdot 10^{-4} \text{ cm}^3/(\text{mole Cu})$ for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ and $\chi_{\text{core}} = -0.66 \text{ cm}^3/(\text{mole Cu})$ for $\text{YBa}_2\text{Cu}_3\text{O}_7$ (see, e.g., Refs. 15 and 31). In those cases, when the authors of the papers cited by us did not themselves separate out the paramagnetic contribution χ_{Pauli} , we made the appropriate correction. It should be mentioned also that in determinations of χ_{Pauli} one can disregard the Landau diamagnetism of the conduction electrons, since the relative contribution of these electrons is proportional to $(1/2)m_0/m^*$, where m_0 is the mass of a free electron and m^* is the effective mass. The effective masses turn out to be quite large, as we shall see subsequently, and therefore the Landau diamagnetism is at most a few percent of the total susceptibility.

The values given for the resistivity are either the values just above the superconducting transition, $\rho(T_c)$, or the value of the resistivity extrapolated to zero temperature, $\rho(\text{res})$.

The data for single crystals also includes results for oriented epitaxial films.

3. ANALYSIS OF EXPERIMENTAL DATA IN THE VICINITY OF T_c

It is natural to try to describe the behavior of the superconducting properties in the vicinity of T_c within the framework of the phenomenological Ginsburg-Landau theory. The free energy density in the anisotropic case is⁷¹

$$F = \alpha(T - T_c)|\Psi|^2 + \frac{b}{2}|\Psi|^4 + \sum_{i=1,2,3} (4M_i)^{-1} \left| \left(-i\hbar\nabla_i - \frac{2e}{c}A_i \right) \Psi \right|^2; \quad (1)$$

where M_i^{-1} are the principal values of the so-called inverse mass tensor. The parameters α , b , and M_i determine the thermodynamic critical magnetic field H_{cm} and the penetration depth. Because the values of these parameters have been measured with insufficient reliability, we shall adopt as the fundamental quantities the discontinuity in the specific heat, ΔC_p , at the superconducting transition

$$\frac{\Delta C_p}{T_c} = \left[\frac{1}{4\pi} \left(\frac{\partial H_{cm}}{\partial T} \right)_{T_c} \right]^2 \quad (2)$$

and the slope of the upper critical magnetic field $(\partial H_{c2}/\partial T)_{T_c}$. The observed anisotropy in the resistivity and in H_{c2} is uniaxial, possibly because of twinning in the a - b crystallographic plane. In principle, the symmetry of the compound $\text{YBa}_2\text{Cu}_3\text{O}_7$ is orthorhombic. In the presence of uniaxial anisotropy

$$H_{c2}^{\parallel} = \sqrt{2} \kappa_{ab} H_{cm}, \quad \frac{H_{c2}^{\perp}}{H_{c2}^{\parallel}} = \left(\frac{M_c}{M_{ab}} \right)^{1/2}, \quad (3)$$

where \parallel and \perp designate the orientation of the magnetic field relative to the c axis. The penetration depth is related to H_{cm} by the relation

$$\delta_{ab}^{-2}(T) = \frac{2\sqrt{2}eH_{cm}}{\hbar c \kappa_{ab}}, \quad \delta_c(T) = \delta_{ab}(T) \left(\frac{M_c}{M_{ab}} \right)^{1/2}. \quad (4)$$

In turn, the coherence parameters of the Ginsburg-Landau theory are

$$\xi_{ab}(T) = \frac{\delta_{ab}(T)}{\kappa_{ab}}, \quad \xi_c(T) = \xi_{ab}(T) \left(\frac{M_{ab}}{M_c} \right)^{1/2}. \quad (5)$$

In the clean limit with extrapolation to $T = 0$ these parameters give, respectively, the dimensions of the pairs in the a - b plane and along the c axis.

The width of the fluctuation region can be estimated, as usual, by calculating the fluctuation correction to the specific heat.⁷² Above T_c

$$C_p - C_p^{(0)} = \frac{T_c^2 \alpha^2}{16\pi^3} \int \frac{d^3k}{[\alpha(T - T_c) + \sum_i (4M_i)^{-1} k_i^2]^2}. \quad (6)$$

In the three-dimensional case

$$C_p - C_p^{(0)} = \frac{T_c^2 \alpha^{3/2} (M_1 M_2 M_3)^{1/2}}{2\pi (T - T_c)^{1/2}}. \quad (7)$$

Comparing this correction to the jump in the specific heat $\Delta C_p / T_c = \alpha^2 / b$, we find that in the three-dimensional case the fluctuations are small for

$$\frac{|T - T_c|}{T_c} > \text{Gi}_{3D} = \frac{T_c M_1 M_2 M_3 b^2}{4\pi^2 \alpha}.$$

Expressing all these quantities in terms of the jump in the specific heat and H_{c2} , we obtain

$$\text{Gi}_{3D} = \frac{\pi}{32} \frac{T_c^2 (\partial H_{c2}^{\perp} / \partial T)^2 |\partial H_{c2}^{\parallel} / \partial T|}{(\Delta C_p)^2 \phi_0^3}, \quad (8)$$

where $\phi_0 = 2\pi\hbar c / 2e$ is the magnetic flux quantum. If the anisotropy is large, for instance because the structure is layered: $M_3 \gg M_1, M_2$, then sufficiently far from T_c , at temperatures T such that

$$M_3 \alpha |T - T_c| \gg \left(\frac{z}{c_0} \right)^2$$

(where c_0 is the length of the unit cell along the c axis, and z is the number of layers in a unit cell), the integration in (6) becomes two-dimensional, and the correction to the specific heat is

$$C_p - C_p^{(0)} = \frac{T_c^2 \alpha z (M_1 M_2)^{1/2}}{2\pi c_0 (T - T_c)}. \quad (9)$$

The Ginsburg criterion in the two-dimensional case is

$$\frac{|T - T_c|}{T_c} > \text{Gi}_{2D} = \frac{z}{4c_0} \frac{T_c |\partial H_{c2}^{\perp} / \partial T|}{\Delta C_p \phi_0}. \quad (10)$$

The temperature T^* of the transition from the three-dimensional regime to the two-dimensional can be nominally defined as the temperature at which the fluctuation corrections to the specific heat (7) and (9) are equal:

$$M_3 \alpha |T^* - T_c| = \left(\frac{z}{c_0} \right)^2,$$

that is, when

TABLE IV. Ginsburg-Landau parameters for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($x \geq 0.15$).

| | κ_{ab} | $\frac{M_c}{M_{ab}}$ | $\frac{ T^* T_c }{T_c}$ | $\delta_{ab}, \text{\AA}$ | $\delta_c, \text{\AA}$ | $\xi_{ab}, \text{\AA}$ | $\xi_c, \text{\AA}$ | Gi_{3D} |
|----------------|---------------|----------------------|-------------------------|---------------------------|------------------------|------------------------|---------------------|---------------------|
| Ceramic | 100 | — | — | 2000 | — | 20 | — | $2 \cdot 10^{-5}$ |
| Single crystal | 12 | 180 | 0.4 | 700 | 10^4 | 58 | 4.3 | $0.5 \cdot 10^{-5}$ |

$$\xi_c(T^*) = \frac{c_0}{2z}. \quad (11)$$

The statement that the superconductivity assumes a two-dimensional nature means only that far from T_c the expansion in the gradients along the c -axis in Eq. (1) is inadequate. For a discussion of this question, see, e.g., Ref. 73.

Thus, the jump in the specific heat at the superconducting transition and the slope of H_{c2} permit a determination of the coherence length and the penetration depth near T_c , the width of the fluctuation region, and the temperature T^* of the transition from the three-dimensional to the layered description of superconductivity.

We shall consider first the situation for the compound based on the lanthanum cuprates. It can be seen from Table I that the jump in the specific heat is

$$\frac{\Delta C_p}{T_c} \approx 15 \text{ mJ/K}^2 \cdot (\text{mole Cu}) \quad (12)$$

with a relative accuracy of about 20%. With the use of expression (2) we find

$$-\frac{\partial H_{c2}}{\partial T} = 1.8 \cdot 10^2 \text{ Oe/K}$$

with an accuracy of about 10%. The width of the resistivity transition is usually about 0.5–2 K, and it increases with the magnetic field. It would appear that the reason for this increase is that the samples are imperfect. As a result the dependence $H_{c2}(T)$ exhibits a great deal of scatter near T_c . For the ceramic $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ samples the average (over the experimental data) slope of the upper critical field is $\partial H_{c2} / \partial T \sim -2.5 \text{ T/K}$, with an accuracy of about 15%. The upper critical field H_{c2} depends on the concentration of Sr, but not very strongly. For the single crystal samples, as far as we know, the upper critical field has been measured only by a single experimental group, so it is difficult to evaluate the reliability of these data. From Table I we have $-\partial H_{c2}^{\parallel} / \partial T = 0.3 \text{ T/K}$, and $-\partial H_{c2}^{\perp} / \partial T = 4 \text{ T/K}$. The results of analyzing the experimental data with the use of formulas (2)–(5), (8) and (11) are shown below in Table IV. The quantities δ and ξ are associated with the corresponding lengths $\delta(T)$ and $\xi(T)$ by the relations

$$\begin{aligned} \xi_{ab,c}(T) &= \xi_{ab,c} \left(1 - \frac{T}{T_c} \right)^{-1/2}, \\ \delta_{ab,c}(T) &= \delta_{ab,c} \left(1 - \frac{T}{T_c} \right)^{-1/2}. \end{aligned} \quad (13)$$

If we use the interpolation formula

$$\delta(T) = \delta(0) \left[1 - \left(\frac{T}{T_c} \right)^4 \right]^{-1/2}, \quad (14)$$

then we find $\delta(0) = 4000 \text{ \AA}$ (for the ceramic), and $\delta_{ab}(0) = 1400 \text{ \AA}$ and $\delta_c(0) = 2 \cdot 10^4 \text{ \AA}$ (for the single crystal).

TABLE V. Ginsburg-Landau parameters of $\text{YBa}_2\text{Cu}_3\text{O}_7$ single crystal.

| κ_{ab} | $\frac{M_c}{M_{ab}}$ | $\frac{ T^* - T_c }{T_c}$ | $\delta_{ab}, \text{\AA}$ | $\delta_c, \text{\AA}$ | $\xi_{ab}, \text{\AA}$ | Gi_{3D} | |
|---------------|----------------------|---------------------------|---------------------------|------------------------|------------------------|------------------|---------------------|
| a 11 | 65 | 0.4 | 335 | 2700 | 30 | 3.8 | $0.3 \cdot 10^{-5}$ |
| b 27 | 11 | ~ 1 | 525 | 1740 | 20 | 6 | $0.8 \cdot 10^{-5}$ |

For the 1-2-3 compounds the jump in the specific heat is (Table II)

$$\frac{\Delta C_p}{T_c} \approx 16 \text{ mJ/K}^2 \cdot (\text{mole Cu}) \quad (15)$$

with a relative accuracy of about 15%. Using (2) we find

$$-\frac{\partial H_{cm}}{\partial T} = 2.4 \cdot 10^2 \text{ Oe/K.}$$

This result differs somewhat from the results of direct measurements⁵⁹ (see Table II), where H_{cm} was obtained by integrating the experimental dependence $M(H)$. The reason for this discrepancy may be that in the analysis of the results in Ref. 59, a somewhat excessive value $\partial H_{c2}/\partial T = 4.6 \text{ T/K}$ was used. Moreover the magnitude of ΔC_p depends on the sample, presumably because of an incomplete transition into the superconducting state over the entire volume of the sample. In those cases where ΔC_p and $M(H)$ were measured simultaneously good agreement was obtained for the two methods.⁷⁰

It has already been mentioned above that the resistivity transition in a field is rather broadened in comparison to that of ordinary superconductors. The slope of $H_{c2}(T)$ should be determined outside the region of broadening of the transition, but in this region the curves of $H_{c2}^{\parallel}(T)$ exhibit a marked positive curvature, so that the slope $H_{c2}^{\parallel}/\partial T$ is not well defined. In Ref. 21, for instance, the slope $-\partial H_{c2}^{\parallel}/\partial T$ varies from 0.37 T/K near T_c to 0.9 T/K about 10 K from T_c . The slope $\partial H_{c2}/\partial T$ outside the region of broadening of the transition was practically constant and equal to -3 T/K . It can be seen from Table III that these data are characteristic of single crystals of $\text{YBa}_2\text{Cu}_3\text{O}_7$. Analysis of these results yields the values listed below in Table V, where the following cases are treated separately: a) $\partial H_{c2}^{\parallel}/\partial T = -0.37 \text{ T/K}$, $\partial H_{c2}^{\perp}/\partial T = -3 \text{ T/K}$, and b) $\partial H_{c2}^{\parallel}/\partial T = -0.9 \text{ T/K}$, $\partial H_{c2}^{\perp}/\partial T = -3 \text{ T/K}$. If we use the interpolation formula (14), then we obtain for the penetration depth at $T = 0$

$$\begin{aligned} \text{a) } \delta_{ab}(0) &= 670 \text{ \AA}, & \delta_c(0) &= 5400 \text{ \AA}, \\ \text{b) } \delta_{ab}(0) &= 1050 \text{ \AA}, & \delta_c(0) &= 3500 \text{ \AA}. \end{aligned}$$

We note that independent estimates of the penetration depth^{30,74,75} give values $\delta(0) \sim (1.5-3) \cdot 10^3 \text{ \AA}$. These estimates, in turn, were obtained from measurements of μ^+ meson spin resonance and also are not very reliable, since the distribution of the magnetic field in the samples was not known accurately.

From Tables IV and V it can be seen that the fluctuation region in the high-temperature superconductors must be quite narrow. The layered nature of the structure is also evident only rather far away from T_c . In estimating the "cross-over" temperature T^* in Tables IV and V, the most favorable

values $z = 1$ for two-dimensional superconductivity were taken for both $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ and $\text{YBa}_2\text{Cu}_3\text{O}_7$. Actually the number of layers in a unit cell coincides closer with the number of Cu atoms, i.e., $z = 2$ for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ and $z = 3$ for $\text{YBa}_2\text{Cu}_3\text{O}_7$. The conclusion that the superconductivity is three-dimensional agrees with the results of an analysis of the fluctuation conductivity in Refs. 76 and 77, but it disagrees with the statements of Refs. 78-80.

To what has already been said let us add the following. The question of the two-dimensionality of the superconductivity has arisen principally out of the observation that in the 1-2-3 compounds, when yttrium is replaced by any rare earth element having a local magnetic moment (Gd, for instance), T_c is practically unchanged. Since these moments are disordered, it is natural to expect a decrease in T_c , as occurs in alloys with paramagnetic impurities. In the phenomenological Hamiltonian (1) there is a gradient term. If we start from the idea of superconductivity that arises in the two-dimensional Cu-O layers, then the three-dimensional transition is provided for by terms of the form $J \sum \Psi_i \Psi_{i+1}^*$, where Ψ_i is the order parameter in a layer. However, even if the electron spectrum is anisotropic in the normal phase but allows for coherent motion of the electrons along the c axis, then the mass tensor is determined mainly by the characteristics of the electron spectrum. In the latter case the anisotropy of the critical fields and the anisotropy of the resistance are related by

$$\frac{H_{c2}^{\parallel}}{H_{c2}^{\perp}} \sim \left(\frac{\rho_{ab}}{\rho_c} \right)^{1/2},$$

which is usually found to be valid. The insensitivity of T_c to the substitution of rare earth elements in the $\text{REBa}_2\text{Cu}_3\text{O}_7$ compounds would appear to be evidence for the "tubular" structure of the electron spectrum due to the directionality and the spatial localization of the electron d functions of the copper atoms and the p orbitals of oxygen.

4. SOME ESTIMATES OF THE MICROSCOPIC PARAMETERS OF HIGH-TEMPERATURE SUPERCONDUCTORS

In the previous section we have seen that the superconducting properties of the new materials are close phenomenologically to the properties of ordinary superconductors. Accordingly, in the analysis of the experimental data on the electronic characteristics of the high-temperature superconductors in the normal phase we shall assume that in these materials too there is somehow a delocalized electron band (this band could also arise as a result of a dopant in a Hubbard state). Evidence for this possibility is, for instance, the metallic character of the conductivity of the single crystals (say, in the a - b plane) and the constant paramagnetic susceptibility above T_c . The "pure" La_2CuO_4 has a hopping-type conductivity⁸¹ but upon doping with strontium the

character of the conductivity and the resistivity change sharply. Along with the data on the Hall effect,⁶⁶⁻⁶⁸ this result may be an indication that with strontium doping the system transforms from an insulating (Mott) state to a state with delocalized electrons. We shall go into this question more thoroughly below. For now we shall try to make a rough estimate of the parameters of the delocalized band.

In the description of the electron spectrum we shall assume that the Fermi surface is cylindrical. Actually, the large anisotropy of the critical magnetic field H_{c2} and the variations that exist in the resistivity and sometimes in the nature of the conductivity in the a - b plane and along the c axis (see e.g., Ref. 52), indicate that the transport properties of the electrons are highly anisotropic. As for the resistance along the c axis it is necessary to say there is not much reliable data. In the early investigations of $\rho_c(T)$ a tendency towards localization was observed [in contrast to $\rho_{ab}(T)$] at temperatures of the order of T_c . More recent experiments (e.g., Refs. 82-84) have shown that $\rho_c(T)$ and $\rho_{ab}(T)$ depend linearly on the temperature.

For a cylindrical Fermi surface the density of states (for a single spin) is

$$\nu(0) = \frac{2m_{ab}}{2\pi c_0 \hbar^2}, \quad (16)$$

where m_{ab} is the effective mass of the band. The Fermi momentum is

$$\frac{p_F}{\hbar} = \left(\frac{2\pi c_0 n}{z} \right)^{1/2}, \quad (17)$$

where n is the carrier concentration. The density of states (16) does not depend on the Fermi momentum; therefore the plasma frequency of the electrons

$$[\omega_p^{(ab)}]^2 = 4\pi e^2 n \nu_F^2 = \frac{4e^2 z E_F}{c_0 \hbar^2} \quad (18)$$

can be expressed directly in terms of the Fermi energy $E_F = p_F^2/2m_{ab}$ and the lattice parameters. Expression (18) allows us to determine the Fermi energy from the experimentally observed values of the plasma frequency.

For $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ the length of the unit cell along the c axis is $c_0 \approx 13 \text{ \AA}$ and $z = 2$ and for the plasma frequency, according to Table I we have 1.7 eV. From this result we find, using (18), $E_F \approx 0.34 \text{ eV}$ for the Fermi energy. The stoichiometric composition La_2CuO_4 has one carrier per primitive unit cell; therefore in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ the band should be about half full. In reality, the situation is more complicated, but the statement does seem to be true for $x > 0.15$ (see Sec. 5). If we adopt this point of view, then for the band width we can take $\Delta E = 2E_F \approx 0.7 \text{ eV}$. For the ratio T_c/E_F we obtain the estimate $T_c/E_F \approx 0.8 \cdot 10^{-2}$.

Similarly, for $\text{YBa}_2\text{Cu}_3\text{O}_7$ we have $c_0 = 11.7 \text{ \AA}$ and $z = 3$, and the plasma frequency is $\omega_p \approx 2.3 \text{ eV}$ (see Tables II and III). We thus find $E_F \approx 0.37 \text{ eV}$ and the band width $\Delta E = 2E_F \approx 0.74 \text{ eV}$. For the ratio T_c/E_F we find a value $\approx 2 \cdot 10^{-2}$. These estimates are evidence in favor of a rather wide delocalized band.

The determination of ω_p from optical data suffers from some well-known uncertainties. In some cases ω_p can be determined by the electron energy loss method: both methods yield similar results.

To determine accurately the carrier concentration in these materials on the basis of Hall effect data is difficult. The Hall coefficient in weak fields depends on the average scattering cross section. When there are carriers of both signs the ratio of the mobilities enters into this quantity. This situation evidently is found in single crystal $\text{YBa}_2\text{Cu}_3\text{O}_7$, where sometimes carriers of both signs are observed in Hall measurements.⁵² Since the mobility depends on the temperature, the Hall coefficient R_H may also depend on the temperature. This sort of behavior of R_H is observed in single crystals of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ and $\text{YBa}_2\text{Cu}_3\text{O}_7$ (see Tables I-III), where R_H decreases as the temperature decreases from 300 K to T_c . At $T = 300 \text{ K}$ we find from the formula $R_H^{-1} = nec$ a carrier concentration $n \approx 10^{22} \text{ cm}^{-3}$, both for the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ and the $\text{YBa}_2\text{Cu}_3\text{O}_7$ single crystals. The concentration $n = 10^{22} \text{ cm}^{-3}$ for the lanthanum compounds corresponds exactly to one carrier per primitive unit cell (that is, two carriers for each unit cell of the Bravais lattice, with a volume $V_0 \approx 1.9 \cdot 10^{-22} \text{ cm}^3$). The estimate $n \approx 10^{22} \text{ cm}^{-3}$ for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ with $x > 0.15$ is thus reasonable. We should point out that for small x the Hall constant depends on x : $R_H \propto x^{-1}$ (Ref. 66); this dependence is discussed below. For $\text{YBa}_2\text{Cu}_3\text{O}_7$, with a unit cell volume $V_0 \approx 1.74 \cdot 10^{22} \text{ cm}^3$, this concentration corresponds to about 1.7 carriers per unit cell. On the other hand, at temperatures of the order of 100 K, experimental results give 1.2-1.5 carriers of each sign per unit cell.⁵² (For our purposes this scatter is not very important, even though for $\text{YBa}_2\text{Cu}_3\text{O}_7$, with $y \approx 6.5$ the Hall coefficient R_H has been found to depend strongly on the oxygen concentration,⁶⁹ in much the same way that it does for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ at small x .) We shall therefore adopt the value $n = 10^{22} \text{ cm}^{-3}$ for the carrier concentration in $\text{YBa}_2\text{Cu}_3\text{O}_7$, although this estimate may prove to be inexact.

We can now, using formulas (16)-(18), estimate the Fermi momentum and the band mass. For $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($x \geq 0.15$) and $\text{YBa}_2\text{Cu}_3\text{O}_7$ we have, respectively,

$$\frac{p_F}{\hbar} \approx 0.64 \cdot 10^8 \text{ cm}^{-1}, \quad \frac{m_{ab}}{m_0} \approx 4.7 \quad (19)$$

$$\frac{p_F}{\hbar} \approx 0.5 \cdot 10^8 \text{ cm}^{-1}, \quad \frac{m_{ab}}{m_0} \approx 2.6. \quad (20)$$

As can be seen from Tables I-III, the Pauli susceptibility has been measured with comparative reliability. It amounts to about $1.5 \cdot 10^{-4} \text{ cm}^3/(\text{mole Cu})$ for the two types of superconducting compounds. From the formula

$$\chi_{\text{Pauli}} = \frac{2\mu_B^2 \nu(0)}{1 + Z_0}, \quad (21)$$

where the factor $(1 + Z_0)^{-1}$ takes into account renormalization due to Fermi liquid exchange effects, it is possible to estimate the effective mass $m^{(\nu)} = m_{ab}/(1 + Z_0)$. We find $m^{(\nu)}/m_0 \approx 7.5$, both for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ and $\text{YBa}_2\text{Cu}_3\text{O}_7$. These effective masses do not depend on the estimate of the carrier concentration. We call attention to the fact that both the susceptibilities per mole of Cu and the effective masses coincide for the two types of compounds. At the same time, the effective masses m_{ab} and $m^{(\nu)}$ are markedly different from each other: the ratio $m^{(\nu)}/m_{ab}$ is equal to 1.6 and 2.9, respectively, for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ and $\text{YBa}_2\text{Cu}_3\text{O}_7$. At the present time it is difficult to say to what extent these facts are

related to the spin correlation of the electrons, how they depend on the estimate of the carrier concentration, on lack of accuracy in the measurement of ω_p , or on other factors.

If we introduce the Sommerfeld constant γ (this is the coefficient of the linear term in the low-temperature specific heat in the normal state)

$$\gamma = \frac{2\pi^2}{3} v(0) (1 + \lambda), \quad (22)$$

where the factor $(1 + \lambda)$ is due to the electron-phonon interaction, then on the basis of the results for χ_{Pauli} we obtain

$$\frac{\gamma}{(1 + \lambda)(1 + Z_0)} \approx 11 \text{ mJ/K}^2 \cdot (\text{mole Cu}) \quad (23)$$

for the two types of compounds. It is interesting to compare this value with the discontinuity in the specific heat $\Delta C_p/T_c$ from (12) and (15). Let us define $\beta(\lambda) = \Delta C_p/T_c \gamma$ as the ratio of the discontinuity in the specific heat to the Sommerfeld constant for the case of a strong electron phonon interaction. In the case of weak coupling, $\beta(0) \approx 1.43$. It is easy to see that

$$\frac{\Delta C_p}{\beta(0) T_c} = 10.5 - 11.2 \text{ mJ/K}^2 \cdot (\text{mole Cu}),$$

which is very close to the value of γ from (23) if all renormalizations are neglected. This fact has been noted in published papers and is a somewhat unexpected result. According to Ref. 85 we have

$$\beta(\lambda) = \beta(0) \left[1 + 1.8 \left(\frac{\pi T_c}{\omega_0} \right)^2 \left(\ln \frac{\omega_0}{T_c} + 0.5 \right) \right] \quad (24)$$

for small values of T_c/ω_0 , where ω_0 is the characteristic phonon frequency. Although the correction can still be considered small for LaSrCuO, in the case of YBa₂Cu₃O₇, for which $T_c \approx 95$ K and $\theta_D \approx 400$ K, it is of the order of unity. To estimate the magnitude of the electron-phonon interaction with the use of formulas like (23) and (24) is difficult, because ω_0 in (24) does not necessarily coincide with θ_D .

Let us turn now to the data on the resistivity. Knowing the resistivity one can determine the mean free path in the usual way:

$$l = \frac{P_F}{\rho n e^2}. \quad (25)$$

Using the values that have been obtained for the Fermi momentum and the carrier concentration, we find

$$l = 27 \left(\frac{\rho_0}{\rho} \right) \text{ \AA} \quad \text{for } \text{La}_{2-x}\text{Sr}_x\text{CuO}_4, \quad (26)$$

$$l = 21 \left(\frac{\rho_0}{\rho} \right) \text{ \AA} \quad \text{for } \text{YBa}_2\text{Cu}_3\text{O}_7,$$

where $\rho_0 = 100 \mu\Omega \cdot \text{cm}$ is taken for convenience as the characteristic value of the resistivity. Comparing expression (26) with the value of ξ from Table IV, we see that even the best samples of La_{2-x}Sr_xCuO₄ with a resistivity $\rho(T_c) \approx 250 \mu\Omega \cdot \text{cm}$ are effectively "dirty." At this resistivity the mean free path in the vicinity of T_c should be of the order of 10 \AA. In the dirty limit of the BCS theory the parameter ξ_{ab} from Table IV is related to $\xi_0 = \hbar v_F / 2\pi T_c$ by the relation $\xi_{ab} = 0.91 (\xi_0 l)^{1/2}$. From this we find $\xi_0 \approx 48$ \AA for the ceramic La_{2-x}Sr_xCuO₄. For single crystal La_{2-x}Sr_xCuO₄ with a resistivity of $250 \mu\Omega \cdot \text{cm}$ (see Table I), we obtain $\xi_{0ab} \approx 400$ \AA. Such a large value of ξ_{0ab} is apparently due to the underestimated value of the slope $|\partial H_{c2}^{\parallel} / \partial T| \approx 0.3$ T/K obtained in Refs. 4 and 44. The idea has been expressed⁶⁵ that the compounds of the LaSrCuO system are clean superconductors. The main argument in Ref. 65 is the statement that the critical magnetic field H_{c2} does not depend on the resistivity of the sample, i.e., on the mean free path. On the other hand, we can conclude from Table I that because of the great amount of scatter in the data for H_{c2} , it is hard to make any judgments regarding the presence or absence of a dependence of H_{c2} on the resistivity.

From Table V and expression (26) it can be seen that the best single crystal samples of YBa₂Cu₃O₇ (with a resistivity $\rho(T_c) < 100 \mu\Omega \cdot \text{cm}$) can be considered as clean. From the BCS theory in the clean limit, $\xi_{ab} = 0.84 \xi_{0ab}$ (and similarly for ξ_c), and we find $\xi_{0ab} = 24-36$ \AA and $\xi_{0c} = 4.5-7$ \AA. Estimates of some microscopic parameters are given in Table VI.

The quantity $\xi_F = \hbar v_F / 2\pi T_c$ can be calculated directly. Taking the effective mass to be $m_{ab}/m_0 = 4.7-7.5$ for La_{2-x}Sr_xCuO₄ (see above) we find $\xi_{0ab} = 37-55$ \AA. For YBaCuO, with an effective mass $m_{ab}/m_0 \approx 2.6-7.5$, we have $\xi_{0ab} = 10-28$ \AA. These estimates, in general are in poor agreement with the values in Table VI.

The most interesting feature of the resistivity of the new superconducting materials is its linear temperature dependence, which is observed in the temperature region immediately above T_c and up to very high temperatures [about up to 1000 K for La_{2-x}Sr_xCuO₄ (Refs. 50 and 65) and to 500 K for YBa₂Cu₃O₇ (Ref. 50)]. If the mean free path is taken in the form $l^{-1} = l_{\text{res}}^{-1} + l_T^{-1}$, where l_T^{-1} is proportional to T , then $l_T(T_c)$ can be estimated from formula (25). We shall discuss the results obtained in Refs. 50 and 65 for La_{2-x}Sr_xCuO₄, where those investigators observed a linear variation in the resistivity up to 1000 K. For the slope $\partial \rho / \partial T = 4 \mu\Omega \cdot \text{cm}$ (Ref. 55), we find $l_T(T_c) \approx 20$ \AA, and for the slope $\partial \rho / \partial T = 3.4 \mu\Omega \cdot \text{cm}$, from Ref. 65, we find $l_T(T_c) \approx 24$ \AA. When the temperature is raised from about 40 K to 1000 K the mean free path decreases by a factor of about 25, to 0.7-0.8 \AA. The product $p_F l / \hbar$ at $T = 1000$ K is

TABLE VI. Some microscopic parameters for the compounds La_{2-x}Sr_xCuO₄ and YBa₂Cu₃O₇.

| | E_F eV | T_c/E_F | ξ_{0ab} , \AA | ξ_{0c} , \AA | n , 10^{21} cm^{-3} | p_F/\hbar , 10^8 cm^{-1} | $\hbar/p_F \xi_{0ab}$ |
|---|-------------|---------------------|----------------------|---------------------|------------------------------------|---|--------------------------------|
| La _{2-x} Sr _x CuO ₄ Ceramic | 0.34 | $0.8 \cdot 10^{-2}$ | 48 | — | 10 | 0.64 | $0.3 \cdot 10^{-1}$ |
| YBa ₂ Cu ₃ O ₇ Single crystal | 0.37 | $2 \cdot 10^{-2}$ | 24 ÷ 36 | 4.5 ÷ 7 | 10 | 0.5 | $(0.6 \div 0.8) \cdot 10^{-1}$ |

equal to approximately 0.5. This value of $p_F l / \hbar$ is, of course quite small. For such small values of this parameter one would expect saturation of the resistivity according to the Ioffe-Regel' rule.⁸⁶ In models where the transport properties of the electrons are assumed to be two-dimensional, the parameter $p_F l / \hbar$, as follows from (17) and (25), is equal to

$$\frac{p_F l}{\hbar} = \frac{2\pi c_0 \hbar}{ze^2 \rho}.$$

Thus, the product $p_F l / \hbar$ is expressed only in terms of the measurable resistivity and the lattice parameters. This product is independent of assumptions regarding the carrier concentration n and of the carrier scattering mechanism and the magnitude of the corresponding interaction. Therefore the absence of saturation for $p_F l / \hbar = 0.5$ may be only an indication that either saturation occurs somewhat later, and the simple expression (25) is not applicable for such short mean free paths (see e.g., Ref. 87), or, more probably, that the measured resistivity is somewhat high (perhaps because of the inhomogeneity of the sample). The slope that was obtained in Ref. 8, for an epitaxial layer of $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$, $\partial\rho/\partial T \cong 1.7 \mu\Omega \cdot \text{cm}$, was a factor of 2 lower, but in this experiment it was not determined to what temperature the linear behavior of $\rho(T)$ was maintained. We emphasize that in contrast to the assertions of Ref. 50, these arguments do not depend on the specific scattering mechanism, and the fact that there is no saturation still does not permit any estimates to be made for the magnitude of the interaction that is involved in the scattering.

The linear dependence of the resistivity has still no good explanation. In addition to the usual phonon mechanism, which, generally speaking, still cannot be ruled out, we can propose the possibility that the linear dependence is due to scattering by centers whose charge fluctuates so as to make the resistivity proportional to the temperature.⁸⁸ Such a linear dependence $\rho(T)$ can also be obtained within the framework of the Anderson model.⁸⁹ Without specifying the nature of all the phenomena, one can, however, arrive at some estimates just from the slope of the resistivity.

First of all it is clear that the linear behavior of the resistivity (at least in the lanthanum compounds) cannot be due to that part of the phonon spectrum near the Debye frequency ($\theta_D \approx 400$ K) and which in principle would be responsible for the superconducting pairing. If we designate by λ the interaction constant for the interaction of the electrons with these phonons, then the linear dependence $\rho(T)$ allows us to find an upper limit to λ . Actually, we set $\hbar v_F l^{-1} = 2\pi T \lambda_{\text{eff}}$, so that λ_{eff} determines the slope of the resistivity, $\partial\rho/\partial T$. As usual, from (25) and the formula $\omega_p^2 = 4\pi n e^2 / m_{ab}$ we can obtain

$$\lambda_{\text{eff}} = \frac{\hbar \omega_p^2}{8\pi^2} \frac{\partial\rho}{\partial T}. \quad (27)$$

Substituting into (27) the values $\omega_p = 1.7$ eV and $\partial\rho/\partial T = 3.4 \mu\Omega \cdot \text{cm}/\text{K}$, we find for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ the value $\lambda_{\text{eff}} \approx 2.4$. The fact that the linear variation of the resistivity in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ is maintained in the range of temperatures of the order of 100–400 K, where the phonons of characteristic energy θ_D should turn on, shows that the interaction constant λ for the interaction of the electrons with the corresponding part of the phonon spectrum is small com-

pared to λ_{eff} . The good linearity of $\rho(T)$ in the region 100–400 K imposes the inequality $\lambda \lesssim 0.1 \lambda_{\text{eff}}$. For $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, therefore, we obtain the estimate $\lambda \lesssim 0.2$. In principle, the linear variation of the resistivity might be due to scattering by phonons with a characteristic energy less than, or of the order of, T_c . Actually, there is a maximum on the curve of $C(T)/T^3$ at $T \approx 20$ K.⁴² It coincides with a peak in the phonon density of states at a phonon energy of about 11 meV, found in neutron measurements of the phonon spectrum.^{81,90} In such a situation λ_{eff} may be related to the constant of interaction with the low-lying part of the phonon spectrum.

In the 1-2-3 compounds $\rho(T)$ is linear in the range from 100 K to 500 K.⁵⁰ Using (27) and the values $\omega_p = 2.3$ eV and $\partial\rho/\partial T = 0.9 \mu\Omega \cdot \text{cm}/\text{K}$ one obtains $\lambda_{\text{eff}} \approx 1.2$. The linear behavior of $\rho(T)$ for these compounds may in principle be due to scattering by phonons with a characteristic energy of the order of $\theta_D \approx 400$ K, since the linearity of $\rho(T)$ begins essentially at $T \gtrsim 0.25 \theta_D$. This event is improbable, however, because for $T \sim \theta_D$ and $\lambda \sim 1$ the scattering by phonons is highly inelastic. As expected, this effect, formally, would lead to a suppression of the superconductivity. One way or another, the linearity of the resistivity implies for $\text{YBa}_2\text{Cu}_3\text{O}_7$ the inequality $\lambda \lesssim \lambda_{\text{eff}}$, from which follows the upper limit $\lambda \lesssim 1.2$.

5. DEPENDENCE ON COMPOSITION AND THE PROBLEM OF THE GROUND STATE

In this section we shall attempt to assess the "quality" and the reliability of the data that have been used above. According to Tables I–III, most of the experimental results for instance, for the discontinuity in the specific heat at the superconducting transition, are grouped around some average values. The scatter in the resistivity data may be ascribed first of all to the various means of preparing the samples and the quality of these samples. For the YBaCuO compounds the experimental measurements of the resistivity along the c axis, $\rho_c(T)$, are indicative of this situation. While $\rho_{ab}(T)$ exhibits a metallic behavior in all investigations, in most of these cases the component $\rho_c(T)$ increases as the temperature is decreased, demonstrating a localized behavior. Only in the work published in Refs. 82–84 and 91 and reported at the recent conference in Interlaken, Switzerland, has it been shown that when the quality of the samples is improved $\rho_c(T)$ takes on the same characteristic linear variation as $\rho_{ab}(T)$. In general, the Pauli susceptibility χ_{Pauli} , the critical field H_{c2} , and others are not very sample-sensitive either in YBaCuO or in LaSrCuO (with substantial doping). Moreover, it is well known now that the situation is considerably more subtle, and a number of physical measurements have shown that some important properties of the new materials depend strongly on their composition. This dependence shows up in a very narrow range of concentrations (near the stoichiometric composition for La_2CuO_4 and for the $\text{YBa}_2\text{Cu}_3\text{O}_y$ compounds, near the composition $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ in oxygen).

In the usual Fermi-liquid picture, the stoichiometric compound La_2CuO_4 must necessarily be metallic, with a half-filled band. Instead, the compound $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ for small x and y (x and y in the 10^{-2} range) shows magnetic properties, in particular antiferromagnetic two-dimensional

and three-dimensional ordering.⁹² In other words, the electrons are sufficiently localized to be characterized by a local moment. It is natural to attribute this circumstance to Coulomb correlations and to consider that the ground state is a Mott insulator. Further introduction of Sr, however, destroys the magnetic ordering and, as is now believed (see, e.g., Refs. 3 and 92), a state arises that corresponds only to a spin glass or a quantum spin liquid. (This state is a candidate for the resonating valence bond state postulated by Anderson in his model). With increasing concentration, $x \gtrsim 0.1$, superconductivity develops. Ordinarily it is believed that the concentration $x \approx 0.15$ is optimum (see, for example, Ref. 93), since T_c has a slight maximum there. A natural question is: what lies hidden behind this statement? In this respect the clearest data are Hall effect data. Briefly, these results may be described in the following way. While the stoichiometric composition La_2CuO_4 indeed corresponds to a Mott insulator, carriers are generated as the material is doped, and in the system $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ the number of holes should be proportional to x , and consequently, for the Hall coefficient we have $R_H \propto x^{-1}$. It has been shown experimentally^{66,68} that this is actually the case for $x < 0.15$. For $x \gtrsim 0.15$, it is found that R_H falls off sharply and the number of carriers increases approximately to that of the stoichiometric composition (1 hole per Cu atom, or $n \approx 10^{22} \text{ cm}^{-3}$) (Ref. 67). It is these concentrations of Sr that we usually had in mind in the discussions above when we attempted to show that as a whole the properties of superconductivity and the picture of the normal state are not at variance with usual notions. It would be interesting to follow the tendency in the behavior of the superconducting properties in the vicinity of $x \sim 0.15$ and smaller values of x in the same sense as they have been analyzed in Sec. 2, but unfortunately, in the existing state of affairs, it is not possible to do so. A sharp change in the Hall coefficient is observed in the $\text{YBa}_2\text{Cu}_3\text{O}_7$ system at $y \approx 6.5$ (Ref. 69). Of course it is tempting to ascribe these phenomena to an insulator-metal transition. If this is the case, then the experimental properties such as the susceptibility, the lattice parameters, and others do not show dramatic changes and evidently no sharp discontinuity in the resistivity has been observed (although the resistivities for the doped and the "pure" La_2CuO_4 samples differ by two orders of magnitude). From these considerations it follows that the insulating state and the metallic phase must be rather close in energy. This transition until now has been discussed as being a function of concentration. If the nature of the phenomena we are dealing with is actually related to the Mott transition, then in this region of concentration one should also study the transition as a function of the temperature.

In recent investigations^{3,94} an attempt has also been made to relate the problem of the low-temperature linear term in the specific heat in the LaCuO system with the doping level. According to these results, the linear term γ^* is not present in the antiferromagnetic phase of the systems $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ and $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$, and then it increases sharply in the transition from $x = 0.02$ to 0.04 . In Ref. 3 it was found that γ^* falls off again towards $x \approx 0.15$.

If the results of Ref. 3 are correct, then they undoubtedly correlate with the schematic phase diagram described above, and at the same time they are difficult to interpret unambiguously as favoring the Anderson model. It should

be noted, however, that low-temperature measurements of the specific heat for $\text{YBa}_2\text{Cu}_3\text{O}_y$, depending on the oxygen concentration have given a linear low-temperature contribution γ^* that is independent of y in the range $y = 7-6$ (Ref. 35). Nevertheless, one cannot at present rule out the possibility that γ^* is due to a small (about 1%) inclusion of a foreign phase (see, e.g., Ref. 95).

6. CONCLUSIONS

Let us bring together those qualitative conclusions that we can arrive at from the preceding analysis. If it is assumed that in doped La_2CuO_4 (or in YBaCu_3O_7) the superconducting properties come about within the context of the usual Fermi-liquid ideas of a rather wide delocalized band, then we find that the width of this band is $\Delta E \sim 0.7 \text{ eV}$, which is comparable with the parameters of organic materials. The scatter in the data at the present time, for instance for ω_p , is quite large, and this estimate is not a final one. Moreover, this value for the width of the band is sufficiently small that pronounced polaron effects could appear in it.⁹⁶ The Fermi-liquid approach also incorporates such characteristics as γ and χ_{Pauli} . Even the estimate of the size of the Cooper pair, $\xi_0 = \hbar v_F / 2\pi T_c$ is in poor agreement with experiment. Concerning our conclusions regarding the nature of the superconductivity in the new materials, it is important to emphasize that from the point of view of the Ginsburg-Landau phenomenology they are well defined three-dimensional anisotropic materials, in which the fluctuation region as previously is relatively narrow, and consequently this conclusion is also in agreement with the picture of a rather wide band (the results of the first sections and of the last one in this sense agree quantitatively). A practical outcome of these considerations is that the theory of superconductivity of the new materials will undoubtedly also be a mean-field model. The layered structure of these compounds, which shows up so surprisingly in the independence of T_c on the replacement of yttrium by rare earth elements with a magnetic moment, does not play a major role near T_c , but far from T_c the formulas for H_{c2} , for instance, should most likely be different from the predictions of the BCS theory. The fluctuation region according to Tables IV and V should be $\Delta T \sim 10^{-2} - 10^{-3} \text{ K}$. It seems to us that for the width of the resistive and magnetic transitions ($0.5-1 \text{ K}$) that is characteristic of most of the samples, it is still too soon to make any judgments regarding any properties that are related to fluctuations. Finally, a simple glance at the data in Tables I-III convinces us that the level of study of the new materials that has been achieved experimentally is far from perfect, and the scatter that exists in, for example, the slope of $H_{c2}(T)$ indicates that the quality of the single crystals is still poor. Accordingly, our estimates and conclusions are still subject to change. The key to all these problems remains the study of the nature of the ground state (in the normal phase) and the dependence on composition. The majority of the data collected in Tables I-III, except for those of the Hall effect experiments, at the present time does not permit us to establish any definite physical laws or relations with possible phase transformations in the oxide superconductors.

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