PHYSICAL REVIEW B VOLUME 36, NUMBER 7 1 SEPTEMBER 1987

Normal-state properties of $A\mathrm{Ba_2Cu_3O_{7-y}}$ compounds (A = Y and Gd): Electron-electron correlations

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(Received 12 June 1987)

Resistivity, thermoelectric power, Hall effect, and magnetic susceptibility measurements are reported in the normal state of the high-T_c compounds $\mathrm{YBa_2Cu_3O_{7-y}}$ and $\mathrm{GdBa_2Cu_3O_{7-y}}$. The results are different from those expected for an uncorrelated metallic band. We suggest that Coulomb interactions are important and that the interaction energy is comparable to or larger than the uncorrelated bandwidth, leading to moderately heavy-fermion-like behavior in the normal state. The Sommerfeld coefficient γ calculated from the susceptibility indicates that the electron-phonon coupling constant at T_c is not unusually large.

There is considerable current interest in the mechanism which may lead to the rather high superconducting transition temperatures in recently discovered oxide superconductors. Several novel mechanisms, most based on strong electron-electron[1] and/or electron-lattice[2] interactions, have been proposed. The importance of electron-electron interactions has been suggested in the $\mathrm{La_2CuO_{4-y}}$ based superconductors,[3] with the parent compound also displaying well-defined magnetic anomalies.[4]

We report resistivity(ρ), Hall effect (R_H), thermoelectric power (S), and magnetic susceptibility (χ) measurements for the normal state of two superconductors, $A\mathrm{Ba_2Cu_3O_{7-y}}$ with A = Y and Gd.[5] Aside from obvious differences in the magnetic susceptibility (a result of the magnetic Gd ion), normal-state properties of the two compounds are similar. However, the transport and magnetic properties are distinctively different from those of simple uncorrelated metals and indicate the importance of electron-electron interactions with no substantial electron-phonon enhancement at T_c. Even with those interactions considered, details of the temperature dependence of the various quantities remain unexplained.

Samples of nominal composition $A\mathrm{Ba_2Cu_3O_{7-y}}$ were prepared by conventional ceramic powder techniques starting with oxides for the Cu and Y or Gd, and barium carbonate. The starting materials were ground and fired three times in oxygen at 900–950 °C to form the superconducting phase, slowly cooled in oxygen, and sintered into the shape of pellets. Transport measurements were performed using conventional dc and/or low-frequency ac techniques, and the magnetic susceptibility was measured with a Quantum Design superconducting quantum interference device (SQUID) susceptometer. All measurements were performed on pieces taken from the same pellet.

In Fig. 1, the normalized resistivity is plotted for both compounds as a function of temperature. The magnitude of the resistivity at room temperature is $\rho \gtrsim 500\ \mu\Omega\,\mathrm{cm}$ in typical well-sintered samples. In all cases, the resistivity decreases linearly with temperature down to $T \sim 120$ K, where it begins to fall more rapidly. From the measurements in Fig. 1, we obtain the transition temperatures $T_c = 92$ and 94.5 K for the Y and Gd compounds, respectively. The transition widths are typically between 0.5 and 2 K from 10% to 90% of the normal resistance. Meissner effect measurements indicate 20% (for Gd) and 40% (for Y) of perfect diamagnetism at 7 K in these sam-

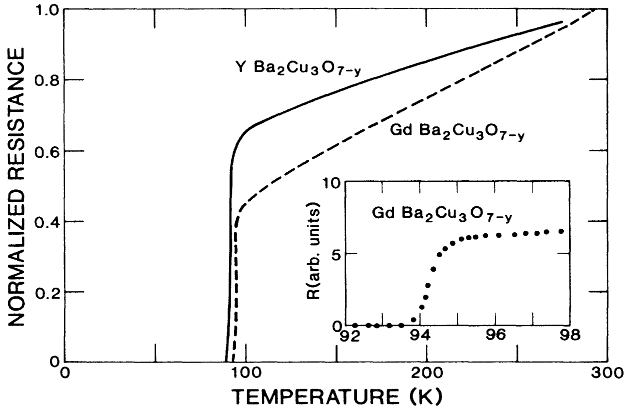

FIG. 1. Resistance, normalized by its value at 300 K, as a function of temperature for $\mathrm{YBa_2Cu_3O_{7-y}}$ and $\mathrm{GdBa_2Cu_3O_{7-y}}$. Typical values for the resistivity of both samples at room temperature are 500 $\mu\Omega\,\mathrm{cm}$ or greater. Higher values for the resistivity are found in less-well-sintered specimens. The inset shows a rather sharp phase transition ($\Delta T_c = 0.6$ K).

ples, while shielding experiments show 90%–100% of $-1/4\pi$.

The Hall coefficient as a function of temperature is shown in Fig. 2 for the Gd compound. The Hall coefficient is more than an order of magnitude larger than that of copper (and with a positive sign) indicating a small number of holelike carriers. The temperature dependence can be well described by $R_H = \text{const}/T$, which in terms of a single-band model suggests the carrier number increases roughly linearly with increasing temperature. Since the Hall coefficient of Y compound shows the same temperature dependence and is the same order of magnitude with the Gd compound, the temperature dependence cannot be explained by skew scattering or the anomalous Hall effect. However, localization of the carriers or a two-band model may explain the behavior.

The thermoelectric power for both materials is plotted in Fig. 3; as expected, $S=0$ in the superconducting state. Above T_c the thermopower is, in both cases, roughly temperature independent and relatively small. From several experiments on these and related compounds, we find a correlation between the magnitude of S and oxygen-defect concentration y. Consequently, we cannot rule out the possibility that the differing magnitudes of S for $YBa_2Cu_3O_{7-y}$ and $GdBa_2Cu_3O_{7-y}$ simply reflect variations in y. Interestingly, the temperature dependence of S (above T_c) is qualitatively similar to that found in strongly correlated electron materials.[6]

The weakly temperature-dependent magnetic susceptibility for two $YBa_2Cu_3O_{7-y}$ samples is displayed in Fig. 4. The small decrease of χ around 240 K is unexplained at present, and the smooth decrease of χ at T_c approached from above may reflect the onset of superconducting fluctuations. The susceptibility curves are representative of several measurements but are in disagreement with the earlier results of Cava *et al.*[7] who found Curie-Weiss behavior. Recent magnetic susceptibility measurements by Junod *et al.*[8] indicate that these earlier results may be associated with the presence of a small amount of second phase, most likely $BaCuO_2$.

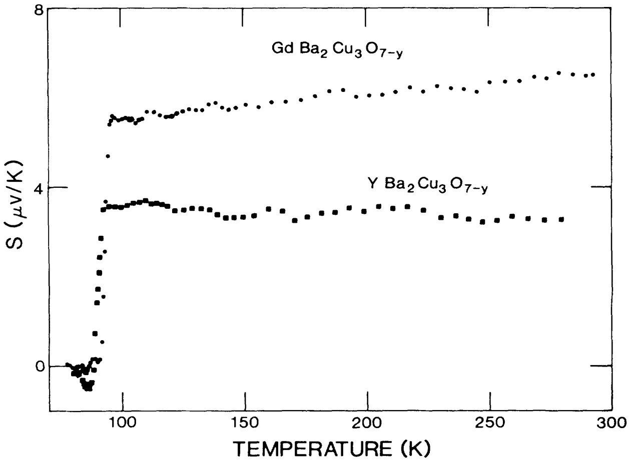

FIG. 3. Thermopower S vs temperature for $YBa_2Cu_3O_{7-y}$ and $GdBa_2Cu_3O_{7-y}$. The decrease of S to zero signals the superconducting transition.

The temperature dependence of the critical field H_{c2} has already been reported.[5] The critical field slope depends on the criterion which defines T_c, with the 90% point giving $dH_{c2}/dT|_{T_c} = 3$–6 T/K and $dH_{c2}/dT|_{T_c} = 1$–1.5 T/K for the 50% point in the two materials.

We analyze the transport and magnetic data in the general way that has proven to be useful for establishing the importance of electron-electron and/or electron-phonon interactions in various groups of materials, such as heavy-fermion systems or linear-chain conductors. Possible anisotropy effects will be neglected. Furthermore, because of the small-band filling, we use free-electron expressions for the various transport and thermodynamic properties, beginning with an estimation of the carrier density which will be needed later.

The room-temperature Hall coefficient gives, through

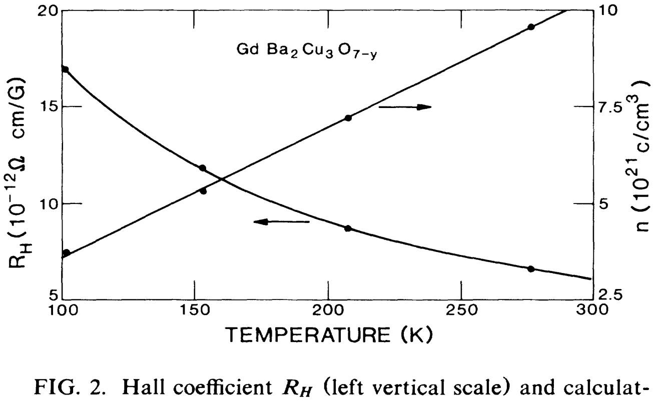

FIG. 2. Hall coefficient R_H (left vertical scale) and calculated carrier density n (right vertical scale) for $GdBa_2Cu_3O_{7-y}$ as functions of temperature. The carrier density is calculated from the single-band expression and lines are drawn as guides for the eyes. $R_H(T)$ can be expressed as const/T when $T > 100$ K (see text). In the measurement, the applied magnetic field ranged from 0 to 8 T.

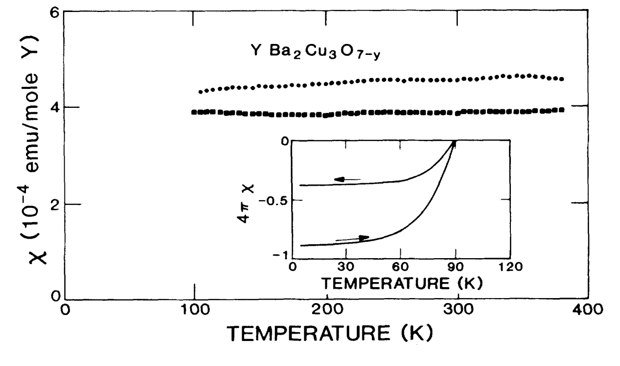

FIG. 4. Measured magnetic susceptibility of two $YBa_2Cu_3O_{7-y}$ samples taken from a single large pellet as a function of temperature. The inset shows results of shielding diamagnetism (temperature increasing) and Meissner effect (temperature decreasing) experiments on one of the samples. Measurements above T_c were performed in a 4-kG applied field and below T_c in 100 G.

the standard expression $R_H=(nec)^{-1}$, 1.7 holes/unit cell, and, consequently, $n \approx 0.6$/Cu site. The composition $A\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$ $(y=0)$ corresponds to $n=0.33$/Cu site by electron counting arguments (A^{3+}, Ba^{2+}, Cu^{2+}, and O^{2-}). At $T=100$ K, we obtain $n=0.2$/Cu site $(y=0.2)$. For an uncorrelated metal with a single wide band, R_H is expected to be temperature independent. The same is true for a correlated-electron band with an on-site Coulomb interaction energy U, the same order of magnitude as the bandwidth $8t$, where t is the transfer integral. Consequently, neither of these descriptions can explain the temperature-dependent Hall constant, although we note that the behavior is not unique (e.g., $R_H \sim T^{-1}$ in the linear-chain conductor tetrathiafulvalene-tetracyanoquinodimethane.[9])

The positive thermopower also demonstrates that conduction is by holes. The overall magnitude and temperature dependence suggest that the materials are not simple uncorrelated metals, for which S would be small and proportional to the temperature. We note that S is also temperature independent in the $(\text{LaBa})_2\text{CuO}_4$ compounds and that this behavior can be explained in terms of rather strong Coulomb correlations.[3]

The mean free path l of the charge carriers can be estimated now from available parameters. The electrical conductivity $\sigma=ne^2l/mv_F$ and Fermi velocity $v_F=(\hbar/m)(3\pi^2n)^{1/3}$ can be combined with the measured quantities ($\rho \simeq 250$ $\mu\Omega$ cm, $n=3.5\times10^{21}/\text{cm}^3$ at 100 K, and $\rho \simeq 500$ $\mu\Omega$ cm, $n=10.2\times10^{21}/\text{cm}^3$ at 300 K) to give mean free paths of 22 and 5 Å for temperatures of 100 and 300 K, respectively. This characteristic length scale is comparable to the unit-cell dimensions. Such a short mean free path is typical of correlated transport, and we will see evidence for this in the thermodynamic properties as well.

The full bandwidth can be estimated from optical measurements of the plasma frequency

$$\omega_p^2=\frac{4\pi ne^2}{m^*} ,$$

together with the carrier density from the Hall constant. Results for the Y compound yield $\omega_p \approx 3$ eV/$\hbar$,[10] giving an *optical* effective mass ratio of $m^*/m=0.5(1.5)$ at $T=100$ K (300 K). The transfer integral

$$t=\frac{\hbar^2}{2m^*a^2},\quad a \sim 4\ \text{Å}$$

is calculated to be $t=2750$ K (for $m^*=m$), so that the *optical* bandwidth (in two dimensions) is $D=8t=3.6$ eV (1.2 eV) at 100 K (300 K).

The nearly temperature-independent magnetic susceptibility of $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ can be interpreted as Pauli paramagnetism in which

$$\chi_p=\mu_B^2\frac{3n}{2\varepsilon_F} .$$

The values of n inferred from Hall measurements lead to calculated values of χ_p (100 K) $=3.6\times10^{-5}$ emu/mole and χ_p (300 K) $=5\times10^{-5}$ emu/mole. Correcting for the core contribution of -1.7×10^{-4} emu/mole results in a measured value of 5.6×10^{-4} emu/mole Y, indicating an enhancement ratio η of the measured susceptibility with respect to the calculated value of

$$\eta=11\ (300\ \text{K})\ \text{to}\ 16\ (100\ \text{K}) ,$$

which is comparable to moderately heavy-fermion compounds such as U_6Fe.[11] This behavior can be described by a renormalized transfer integral t' (and associated bandwidth) through

$$t'=t/\eta=14\ \text{meV}\ (T=300\ \text{K})\ \text{to}\ 28\text{meV}(T=100\ \text{K}) .$$

Although direct measurements of the Sommerfeld coefficient γ are not available, the free-electron expression $\gamma=\pi^2k_B^2\chi_p/3\mu_B^2$ gives 40 mJ/mole Y K^2 calculated from the measured susceptibility. This agrees qualitatively with γ estimated from the specific-heat jump at T_c,[8] $\gamma=27$ mJ/mole Y K^2. The temperature dependence of the upper critical field in the dirty limit is $dH_{c2}/dT=4.48\times10^4\gamma\rho$ (G/K). Taking $\rho=250$ $\mu\Omega$ cm and $dH_{c2}/dT=3$T/K leads to 28 mJ/mole K^2, again in quite good agreement with previous estimates. We conclude that the magnetic susceptibility and the Sommerfeld coefficient are enhanced by a similar amount and that the Wilson ratio (for $T \simeq T_c$) is close to unity (also true in many heavy-fermion systems).

We find that the positively charged carriers in the oxide superconductors have a large, temperature-dependent effective mass, together with a rather small mean free path. Both of these properties are consistent with correlated electron behavior. The Coulomb correlation $1-\eta^{-1}=\frac{1}{2}Un(\varepsilon_F)$ gives for the on-site repulsion $U=5$ eV (3.5 eV) at 100 K (300 K), which is comparable with the bandwidth and could be checked by optical methods as, for example, in the organic conductors.[12] The paramagnetic susceptibility and Sommerfeld coefficient are enhanced by approximately the same amount. If electron-phonon interactions are important in these materials, we expect γ to be enhanced relative to χ_p by a factor $(1+\lambda)$, where λ is the usual electron-phonon coupling constant. Therefore, our results suggest that λ at $T \simeq 100$ K is not much greater than order unity. We note that within the framework of theories of conventional superconductivity, large values for the electron-phonon coupling (~ 10) would be required to account for superconductive pairing at temperatures approaching 100 K.[13] In this same context we should point out that electron-phonon coupling is expected to be a strongly decreasing function of T/Θ_D so that at $T=0$, λ could be considerably larger than unity.[14]

Finally, we note that the necessarily crude analysis employed neglects several important factors, among these anisotropy effects are probably the most important, together with possible two-band effects which may explain the temperature dependence of the Hall constant and thermopower. These factors, however, do not modify our main conclusion about the importance of electron-electron correlations which are central to several emerging theories[15] of superconductive pairing in these materials.

Work at Los Alamos was performed under the auspices of the U. S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Science. Work at the University of California at Los Angeles was supported in part by National Science Foundation Grant No. DMR 87-8620340. One of us (G.L.W.) thanks the Center for Materials Science for supporting his stay at Los Alamos.

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[1] P. W. Anderson, Science **235**, 1196 (1987); S. A. Kivelson, D. S. Rokshar, and J. P. Sethna (unpublished).

[2] C. M. Varma, S. Schmitt-Rink, and E. Abrahams, Solid State Commun. (to be published); P. Prelovsek, T. M. Rice, and F. C. Zhang (unpublished).

[3] R. L. Greene, H. Maletta, T. S. Plaskett, J. G. Bednorz, and K. A. Müller, Solid State Commun. (to be published); J. R. Cooper, B. Alavi, L.-W. Zhou, W. Beyermann, and G. Gruner, Phys. Rev. B **35**, 8794 (1987).

[4] Y. Yamaguchi, H. Yamauchi, M. Ohashi, H. Yamamoto, N. Shimoda, M. Kikuchi, and Y. Syono, Jpn. J. Appl. Phys. **26**, L447 (1987).

[5] Z. Fisk, J. D. Thompson, E. Zirngiebl, J. L. Smith, and S-W. Cheong, Solid State Commun. **62**, 743 (1987); J. O. Willis, Z. Fisk, J. D. Thompson, S-W. Cheong, R. M. Aikin, J. L. Smith, and E. Zirngiebl, J. Magn. Magn. Mater. **67**, 1139 (1987).

[6] See, for example, U. Gottwick *et al.*, J. Magn. Magn. Mater. **63&64**, 341 (1987).

[7] R. J. Cava, B. Batlogg, R. B. van Dover, D. W. Murphy, S. Sunshine, T. Siegrist, J. P. Remeika, E. A. Rietman, S. Zahurak, and G. P. Espinosa, Phys. Rev. Lett. **58**, 1676 (1987).

[8] A. Junod, A. Bezinge, T. Graf, J. L. Jorda, J. Muller, L. Antognazza, D. Cattani, J. Cors, M. Decroux, O. Fisher, M. Banovski, P. Genoud, L. Hoffmann, A. A. Manuel, M. Peter, E. Walker, M. Francois, and K. Yvon, Europhys. Lett. (to be published).

[9] J. R. Cooper *et al.*, J. Phys. (Paris) **38**, 1097 (1977).

[10] J. Orenstein *et al.* (unpublished).

[11] See, for example, G. R. Stewart, Rev. Mod. Phys. **56**, 755 (1984).

[12] J. Torrance, B. A. Scott, and F. B. Kaufman, Solid State Commun. **17**, 1369 (1975).

[13] D. Scalapino (private communication).

[14] G. Grimvall, *The Electron-Phonon Interaction in Metals* (North-Holland, Amsterdam, 1981), p. 125.

[15] T. M. Rice (unpublished); A. E. Ruckenstein, P. J. Hirschfeld, and J. Appel (unpublished).