PHYSICAL PROPERTIES OF HIGH TEMPERATURE SUPERCONDUCTORS I

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NORMAL STATE TRANSPORT AND ELASTIC PROPERTIES OF HIGH T_c MATERIALS AND RELATED COMPOUNDS

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Normal state experiments in high T_c superconductors have given a rich and very confusing story. The confusion stems from the sensitivity to processing history and other sample-dependent effects, from the intrinsic richness of phenomena available in these systems, and from the difficulty of reconciling the unexpected phenomena with any single unifying theory. Most of the data, from pressed powder ("ceramic") samples, represent an exceedingly complicated and sample-dependent average of the different tensor components of the microscopic transport coefficients. Therefore we shall focus on single crystal results whenever possible. The experiments to be discussed are

1. Resistivity
2. Hall coefficient
3. Thermopower
4. Magnetism
5. Ultrasound
6. Thermal conductivity. This is also nicely reviewed by Fischer, Watson, and Cahill,[1] who also review specific heat and electrical resistivity;
7. Electrodynamics

I. Resistivity

Most high T_c superconductors are orthorhombic and thus have 3 independent tensor components for the resistivity, $\rho_{xx} = \rho_a$, $\rho_{yy} = \rho_b$, $\rho_{zz} = \rho_c$. We use a notation where the CuO_2 planes lie in the ab or xy plane, and the CuO chains (in $YBa_2Cu_3O_7$) lie in the b or y direction. However, almost all orthorhombic crystals are microtwinned, so that only an average of ρ_a and ρ_b (called ρ_{ab}) can be measured. It is suspected that ρ_a and ρ_b will differ by less than a factor of 2, so the in-plane average should not be far from an arithmetic mean $(\rho_a + \rho_b)/2$. By contrast, ρ_c is typically larger by a factor of 50 or more.

For homogeneous single-phase samples which are superconducting, the following general features are seen in the normal-phase temperature dependence:

(i) ρ_{ab} is "metallic" with $d\rho_{ab}/dT$ positive and comparable to ρ_{ab}/T.

(ii) ρ_c is larger by $\sim 10^2$ and usually "non-metallic" ($d\rho_c/dT < 0$).

(iii) ρ_{ab} is surprisingly close to linear in T, and the extrapolated value $\rho_{ab}(T=0)$ is close to zero.

(iv) The slope $d\rho_{ab}/dT$ is large, ~ 0.5–1.0 $\mu\Omega$cm/K, corresponding to room-temperature resistivities of 150–300 $\mu\Omega$cm. However, variations of a factor of 2 or more in slope are commonly seen from sample to sample, reflecting problems such as microcracks or inhomogeneities which diminish the effective conducting cross-sectional area, problems with attaching leads, or possibly other factors.

These four observations will now be illustrated with data selected from the literature. Figure I.1 shows resistivity[2] of the non-superconducting "parent" compound La_2CuO_4, an antiferromagnetic
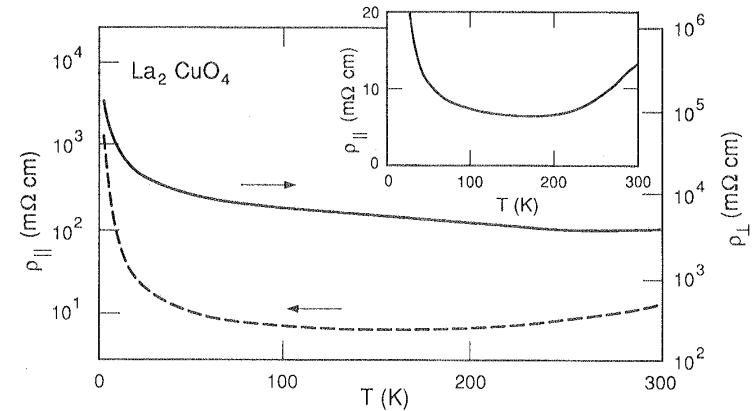

Fig. I.1 ρ_{ab} (denoted $\rho_{\parallel}$) and ρ_c (denoted $\rho_{\perp}$) of insulating La_2CuO_4 from Ref. 2. The inset shows ρ_{ab} on a linear scale.

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insulator. At 300 K, ρ_{ab} is 1.3 x 10^4 $\mu\Omega$cm, and ρ_c is larger by a factor of 300. Both directions show a dramatic increase in $\rho(T)$ at low temperatures. This is interpreted[2] as a crossover from diffusive transport at high temperature to strongly correlated variable range hopping at low temperature. Good homogeneous single crystals of superconducting La$_{2-x}$M$_x$CuO$_4$ (where M = Ca, Sr, Ba) have been hard to grow, and fewer single-crystal resistivity data are available. Figure I.2 shows results for $\rho_{ab}(T)$ from Suzuki and Murakami[3] in a sample which is superconducting at 12 K.
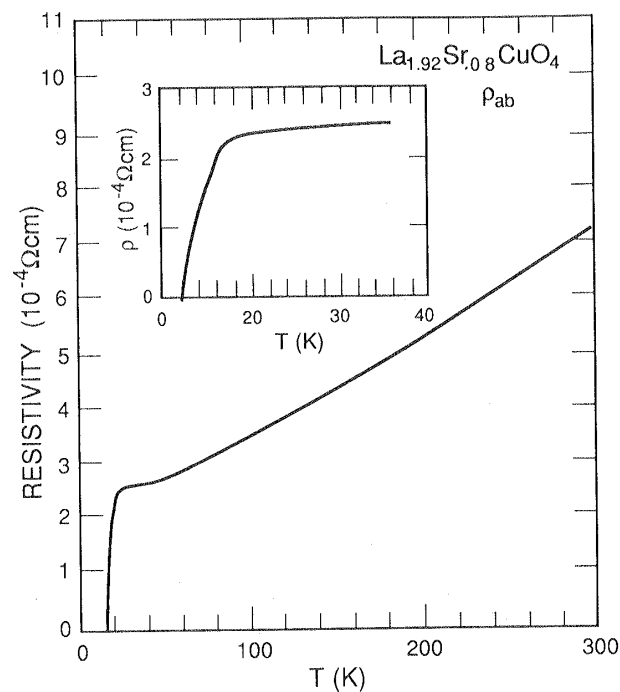
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Superconducting single crystals of the family MBa$_2$Cu$_3$O$_{7-\delta}$ are more common, where M = Y or various Lanthanides, and δ is most often ~ 0. Figure I.3 shows single crystal measurements by Penney et al.[4] on YBa$_2$Cu$_3$O$_7$. Notice that there are two $\rho_{ab}(T)$ curves on two different crystals. The one with the higher T$_c$ shows a lower ρ_{ab}, both in slope (~0.7 $\mu\Omega$cm/K) and in extrapolated $\rho_{ab}(T = 0)$ (~20 $\mu\Omega$cm) compared with the lower T$_c$ crystal (~1.5 $\mu\Omega$cm/K). By contrast, consider the results of Störmer et al.[5] on oriented thin films, shown
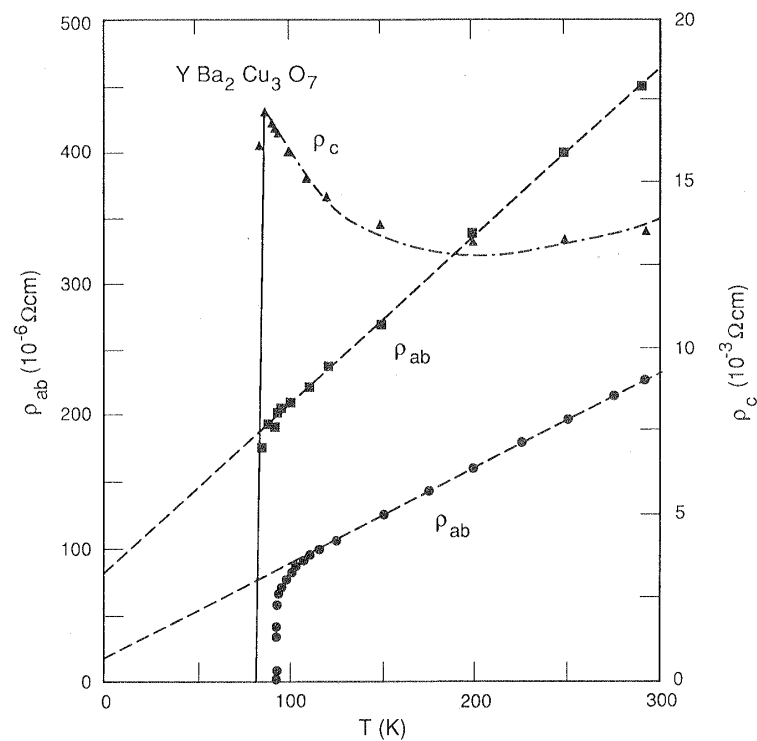
Fig. I.2 $\rho_{ab}(T)$ from Ref. 3, measured on a single-crystal thin film of La$_{1.92}$Sr$_{.08}$CuO$_4$.

Fig. I.3 $\rho_{ab}(T)$ and $\rho_c(T)$ for YBa$_2$Cu$_3$O$_7$ from Ref. 4. The two $\rho_{ab}(T)$ curves are from different crystals.

in Fig. I.4. Here the "best" sample (as measured by T_c and critical current density) has the <u>lowest</u> resistance ratio (3.4 for sample 1 as opposed to 5.4 for sample 6) as well as the highest $\rho(300\ K)$ (233 $\mu\Omega$cm, similar to the better sample in Fig. I.3, for sample 1,
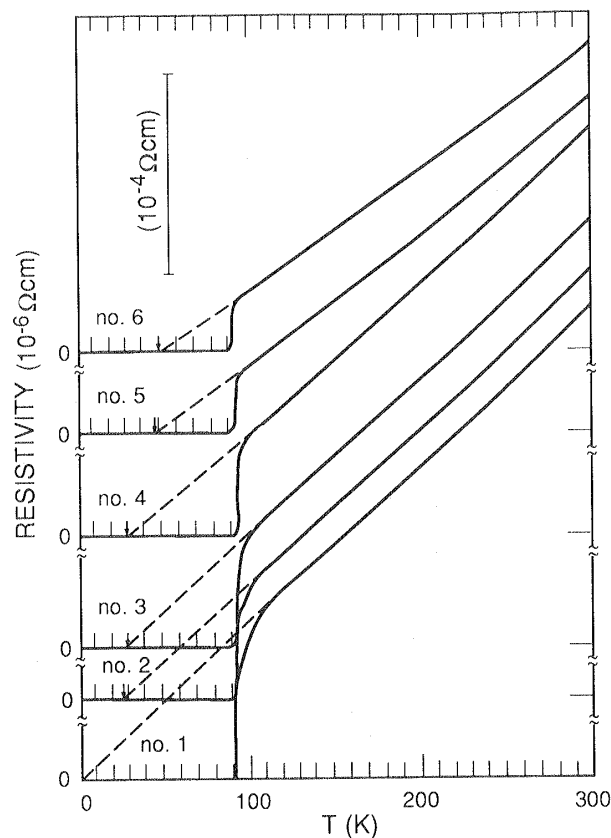

Fig. I.4 $\rho(T)$ for oriented thin films of $YBa_2Cu_3O_7$, from Ref. 5.
Presumably the results are very similar to $\rho_{ab}(T)$ of
single crystals. Samples numbered 1 through 6 have
decreasing values of T_c and j_c.

compared to 151 $\mu\Omega$cm for sample 6.) Furthermore, the best sample (No. 1) has an extrapolated $\rho(0\ K)$ of 0 $\mu\Omega$cm, whereas the worst sample (no. 6) has an extrapolated $\rho(0\ K)$ = -30 $\mu\Omega$cm.

More recently, single-crystal data for other layer structure CuO-based superconductors have become available. Figure I.5 shows results by Martin et al.[6] for an untwinned orthorhombic crystal of $Bi_2Sr_{2.2}Ca_{0.8}Cu_2O_8$ with $T_c \sim 81$ K. Three unusual features should be noted: (i) The anisotropy ρ_c/ρ_a and ρ_c/ρ_b is extremely large, nearly 10^5. This reflects the large spacing of 12 A between CuO layers in the crystal structure. (ii) The "non-metallic" behavior $d\rho_c/dT < 0$ is almost absent. (iii) ρ_a and ρ_b exhibit quite linear temperature dependences, with anisotropy $\rho_a/\rho_b \sim 1.5$-2.0 and extrapolated $T = 0$ intercepts $\rho_b(0) \sim +5$ $\mu\Omega$cm and $\rho_b(0) \sim -15$ $\mu\Omega$cm. The average slope, $d\rho_{ab}/dT$, is 0.46 $\mu\Omega$cm/K.
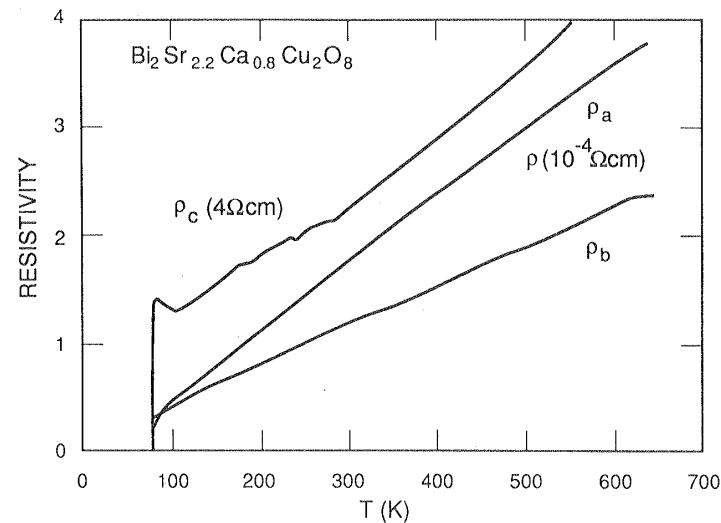

Fig. I.5 $\rho_a(T)$, $\rho_b(T)$, and $\rho_c(T)$ for $Bi_2Sr_{2.2}Ca_{0.8}Cu_2O_8$ as
measured in Ref. 6.

Perhaps the most striking aspect of these data is the surprising degree of linearity of $\rho_{ab}(T)$. The linearity persists up to 600 K as shown in Fig. I.5, and has been followed up to 1100 K in $La_{2-x}Sr_xCuO_4$ and 800 K in $YBa_2Cu_3O_7$ by Gurvitch and Fiory.[7] Of course, conventional metals also have linear $\rho(T)$ curves at higher temperature where the cross section $\sigma \propto \langle u^2 \rangle$ (for scattering degenerate-electron quasiparticles from lattice displacements u) goes as $n + 1/2$ (where n is the Bose occupation factor), which equals $(k_BT/\hbar\omega)$ $(1+1/12$ $(\hbar\omega/k_BT)^2 + \ldots)$ at high temperature. Actually, it is not generally appreciated at how low a temperature the Bloch-Gruneisen resistivity begins to appear linear. This linear resistivity is partly due to the factor of 1/12 and is partly due to other factors. A good example is rhenium,[8] shown in Fig. I.6. These data show the typical weak anisotropy of an hcp metal, and the typical linearity down to $T \sim 75$ K, in spite of a high $\theta_D \sim 420$ K (derived from elastic constants.) The slope $(d\rho/dT \sim 0.065~\mu\Omega cm/K)$ and linearly extrapolated intercepts $(\rho(0~K) \sim -3~\mu\Omega cm)$, are typical of good metals (i.e. metals with propagating electronic quasiparticles, having room-temperature mean free path $\gtrsim 20$ A.) Therefore, it is certainly not correct to cite the linear $\rho(T)$ behavior as a priori evidence for unusual physics. In particular, $\rho_{ab}(T)$ for $La_{1.92}Sr_{0.08}CuO_4$ shown in Fig. I.2 has just the kind of deviation from linearity expected in ordinary metals, and Bloch-Gruneisen-type fits have been made[9] to the data of Figs. I.2 and I.3.

Nevertheless, there are reasons for arguing that the linear $\rho(T)$ is very unusual, and weaker but still plausible reasons for supposing that the extrapolated $T = 0$ value $\rho(0~K) \sim 0$ is in fact "intrinsic" (i.e. characteristic of the best samples). These reasons have been presented by Stormer et al.[5] based on the data of Fig. I.4 and a correspondingly unusual temperature-dependence of the Hall coefficient (to be discussed in the next section.)

A critical test would be to discover metallic samples where $\rho(T)$ can be measured to much lower temperatures, to search for curvature of $\rho(T)$, which would be expected for a conventional phonon scattering mechanism. Such a material has been studied by Xiao et al.[10] and is
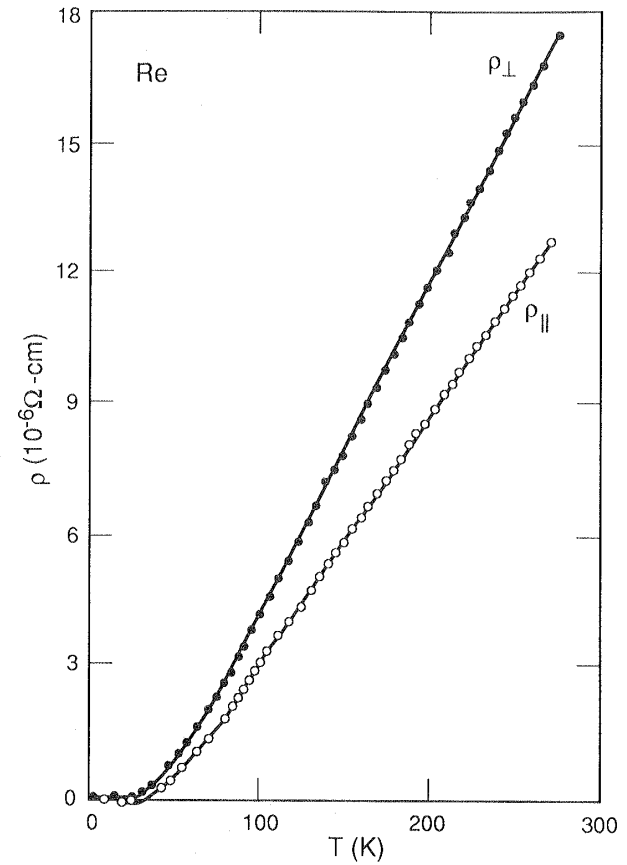

Fig. I.6 $\rho_{ab}(T)$ (denoted as $\rho_\perp$) and $\rho_c(T)$ (denoted as $\rho_\parallel$) for Re metal, from Ref. 8.

shown in Fig. I.7. It is striking that in the best superconductors
(with composition near $BiSrCuO_y$) the $\rho(T)$ curve is linear down to
$T_c \sim 7$ K. The absolute values of $\rho(300$ K$)$ in these polycrystalline
samples are 2–3 x 10^3 $\mu\Omega$cm, much higher than $\rho_{ab}(300$ K$)$ of single
crystals of other superconductors, but typical for polycrystalline
metals. The value of A is remarkably close to zero in good samples.
However, the occurrence of negative values of A in extrapolated cases
is not easy to understand unless the intrinsic $\rho(T)$ behavior is a
highly nonlinear function of T at low T.

It has not been easy to find a theoretical explanation for an
However, counter-examples can be found. For example, Torrance
et al.[11] have studied various metallic but non-superconducting
compounds based on CuO and find ordinary-looking curved $\rho(T)$
behavior. However, their best data were obtained from a compound
$La_4BaCu_5O_{13}$ which does not have a layer structure. Less easily
explained away is a measurement by Cheong et al.[12] on a single
crystal of $La_{1-x}Sr_xCuO_4$ (x $\sim$ 0.02), shown in Fig. I.8. $\rho_{ab}(T)$
appears to have a small low-temperature linear slope, and a fairly
ordinary upward curvature.

It has not been easy to find a theoretical explanation for an
intrinsic linear behavior of $\rho(T)$. Zou and Anderson[13] gave a
plausibility argument based on RVB theory, but their argument has
received criticism.[14] If the behavior is intrinsic, it may not be
limited to CuO systems. Gurvitch[7] has pointed out that similar
behavior was seen[15] in NbO. Figure I.9 shows $\rho(T)$ for various
polycrystalline samples of cubic NbO in the range 77 K < T < 900 K.
Except for being smaller in magnitude by a factor 2–10, the $\rho(T)$ data
for this low-T_c oxide are very reminiscent of the best data for
high-T_c CuO systems. The data are also quite reminiscent of the
behavior of conventional Fermi liquid metals like Re (Fig. I.6).
Another low T_c oxide superconductor is spinel-structure $Li_{1+x}Ti_{2-x}O_4$.
Resistivity data[16] for ceramic samples are shown in Fig. I.10. Again
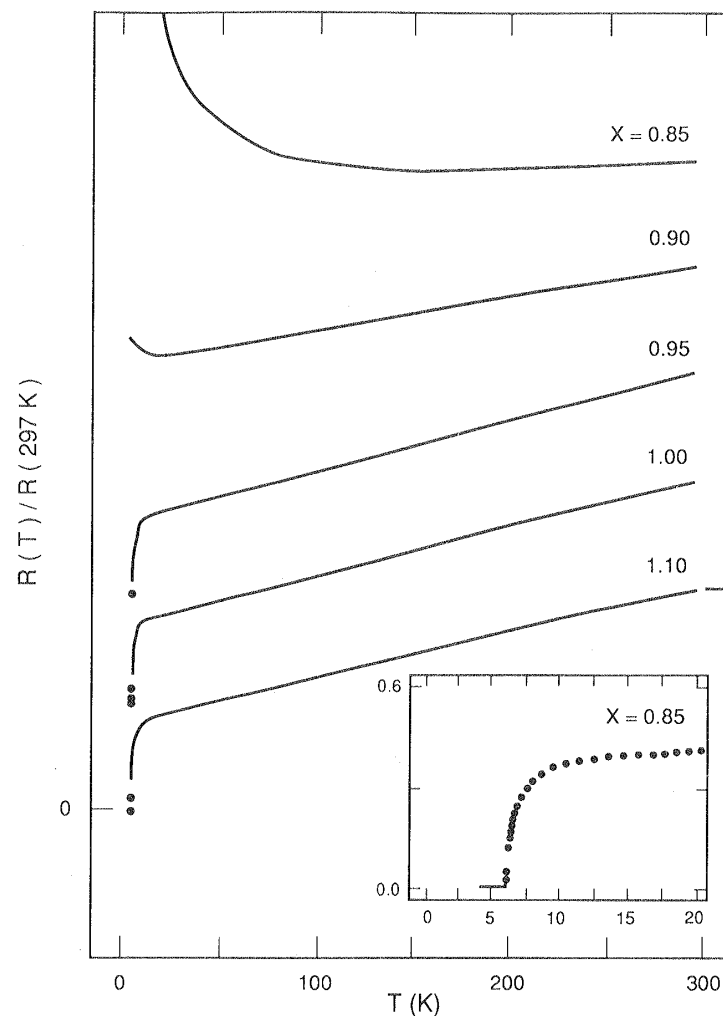the data are reminiscent of the high-T_c CuO superconductors, except

Fig. I.7 $\rho(T)$ for ceramic samples of $Bi_{2-x}Sr_xCuO_y$ for various
values of x, from Ref. 10.

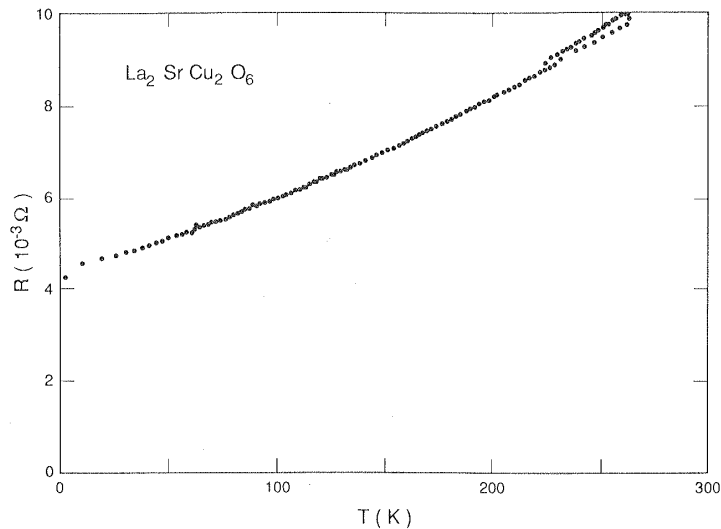Fig. I.8 ρ_{ab}(T) for La$_2$SrCu$_2$O$_6$ from Ref. 12.

that data on high-T$_c$ samples with good metallic conductivity
(ρ < 10^3 $\mu\Omega$cm) are not available.

A second question which the single crystal ρ(T) data raise is
whether the rapid increase as temperature is lowered at low
temperature is intrinsic, and how to explain it. Zou and Anderson[13]
offered an explanation for intrinsic ρ_c ~ 1/T behavior from RVB
theory. Very often data fit well the form ρ_c(T) = A/T + BT where the
term BT is interpreted as arising from defect-related short circuits
of the barriers between CuO$_2$ planes. This is illustrated in Fig.
I.11, which shows data by Hagen et al.[17] plotted as ρ_c(T) versus T^2.
However, Iye et al.[18] have reported on some samples where ρ_c(T) lacks
completely the A/T term, and these are presumed to be the best
annealed crystals. These data are shown in Fig. I.12. Ossipyan
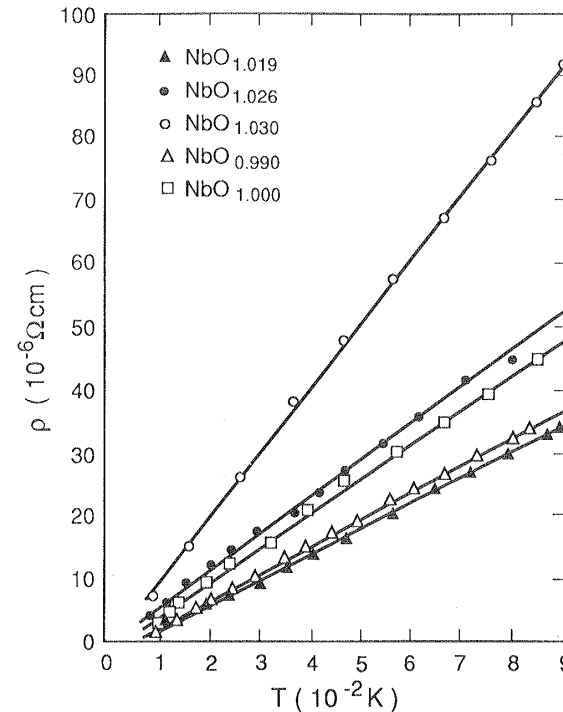et al.[19] have also seen "fully metallic" behavior of ρ_c(T).

Fig. I.9 ρ(T) for cubic NbO$_x$ from 77 to 900 K and various oxygen
stoichiometries near x = 1 (from Ref. 15).

If dρ_c/dT < 0 at low temperature is not intrinsic as Iye suggests,
then this behavior may indicate incipient strong or weak localization
in the c-direction. This explanation has not found immediate
theoretical support. At T = 0 K, strong localization in the
c-direction is inconsistent with delocalization in the ab plane.
Impurity fluctuations in the hopping matrix element t$_c$ will always
permit the wave function to couple better to adjacent planes at
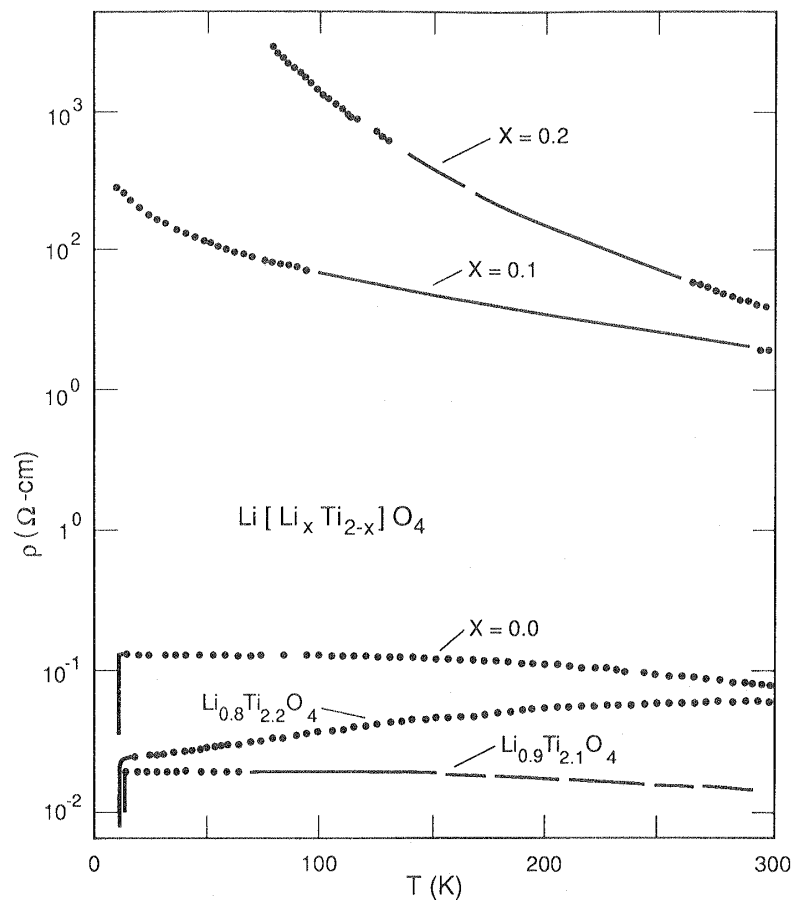certain "hot spots," destroying strong 1D localization.

Fig. I.10 $\rho(T)$ for ceramic samples of spinel structure $Li_{1+x}Ti_{2-x}O_4$ (from Ref. 16).

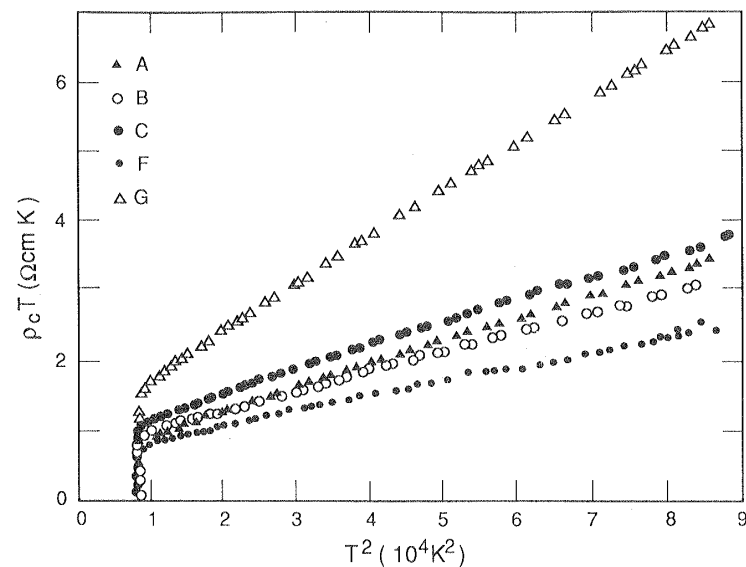Fig. I.11 $\rho_c(T)$ for five single crystals of $YBa_2Cu_3O_7$, plotted as $\rho_c T$ versus T^2 (from Ref. 17).

Finally, it is worth comparing such behavior with that of a more conventional layer-structure superconductor. Single crystal data[20] for the hexagonal-structure, 2.5 K superconductor 4Hb-polytype of TaS_2 are shown in Fig. I.13. The metallic behavior of ρ_{ab} and non-metallic $\rho_c(T)$ are quite similar to that of CuO superconductors. At $T \lesssim 25$ K, the sharply rising $\rho_c(T)$ stops rising and seems to saturate, consistent with weak localization.

A third issue raised by the $\rho(T)$ data is the absence of "saturation" effects. Many metallic d-band compounds are known where $\rho(T)$ appears conventional (i.e. Bloch-Gruneisen-like) at low temperature, but approaches approximately a constant high temperature value, $\rho_{sat} \sim 150$ $\mu\Omega$cm. This was first emphasized by Fisk and
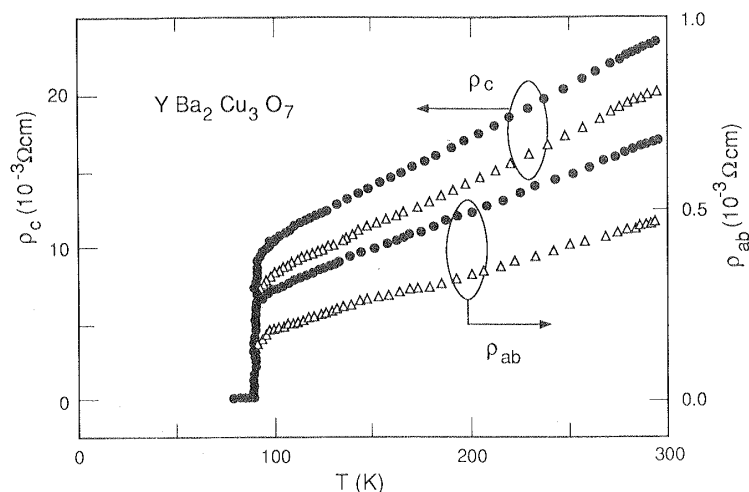
Fig. I.12 ρ_{ab}(T) and ρ_c(T) for a single crystal of YBa$_2$Cu$_3$O$_7$. The two sets of data are obtained from different combinations of contacts. Note that ρ_c(T) is linear in T (from Ref. 18).

Webb,[21] and their data for A15-structure metals is shown in Fig. I.14. The phenomenon does not depend on whether the metal is a good (like Nb$_3$Sn) or bad (like Nb$_3$Sb) superconductor, only on the fact that ρ is large.[21] It is apparent that the carriers at low temperature have a fairly large mean free path, permitting a conventional Fermi liquid analysis, whereas at high temperature the scattering is so strong that the mean free path is $\lesssim$ 3 A. In this regime, wave vectors, velocities, and mean free paths can no longer be properly defined. The experimental observation is that ρ(T) saturates in this regime, and this is often explained by the statement that the mean free path cannot become any shorter than ~3 A, so the resistivity must cease growing. In fact, there is no good theory to explain this.[22] The downward curvature of ρ_{ab} in TaS$_2$ (Fig. I.13) is
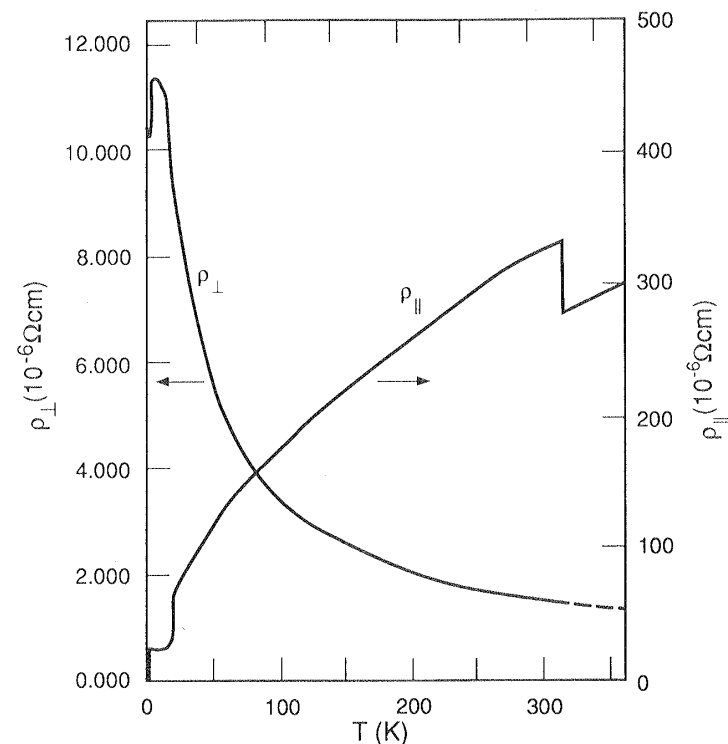
Fig. I.13 ρ_{ab} (denoted as $\rho_{||}$) and ρ_c(T) (denoted as $\rho_{\perp}$) for a single crystal of 4Hb-TaS$_2$ (from Ref. 20).

strongly suggestive of saturation with ρ_{sat} ~ 400 $\mu\Omega$cm. The question is, why are very similar effects not seen in CuO superconductors? In fact, such effects probably are seen in samples where alloying has disordered the CuO$_2$ planes. Figure I.15 shows ρ(T) data[23] for ceramic samples of YBa$_2$(Cu$_{1-x}$Ga$_x$)$_3$O$_7$. As x increases to 0.07, ρ has increased in magnitude by a factor of 2-3 at room temperature, and downward curvature is starting to be noticeable. The crossover point

Fig. I.14 $\rho(T)$ for A15 structure metals showing high T "saturation" (from Ref. 21).

Fig. I.15 $\rho(T)$ for ceramic samples of $YBa_2(Cu_{1-x}Ga_x)_3O_7$ for various values of x, from Ref. 23.

where deviations from Bloch-Gruneisen behavior start to be seen is typically 10 Å. This suggests that pure $YBa_2Cu_3O_7$ has a mean free path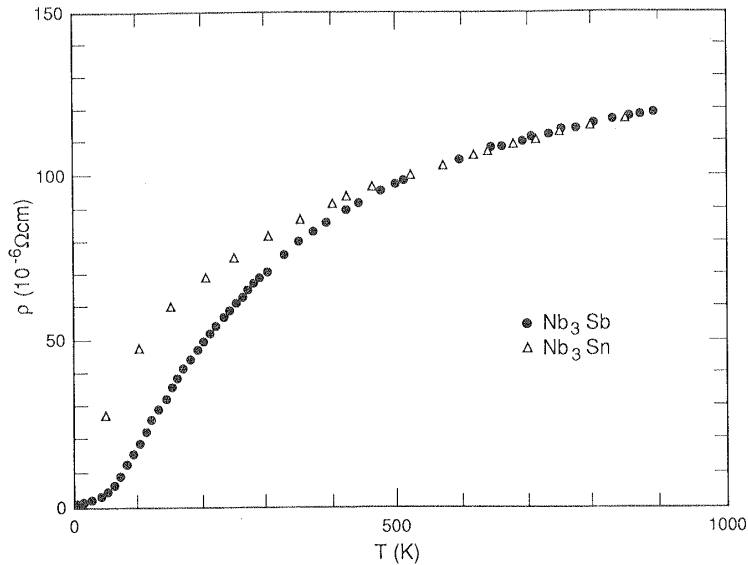 at 300 K of ~ 30 Å. This is consistent with the observed[7] lack of saturation up to 800 K in pure samples. Such a long mean free path is surprising in a high T_c material, since most scenarios derive superconductivity from interactions between quasiparticles, and these interactions should cause scattering.

If we assume a mean free path $\ell \sim 30$ Å at 300 K in $YBa_2Cu_3O_7$, and take quite a low value, $\rho_{ab}(300\ K) \sim 220\ \mu\Omega cm$, we can estimate the number of carriers by a crude argument. We write $\rho = \hbar k_F/ne^2\ell$ and assume that the carriers are located in a single-sheeted cylindrical Fermi surface of radius $k_F = \sqrt{2\pi nc}$ where n is the carrier density and

c is the unit cell height. The resulting value of n corresponds to ~ 1.6 carriers per formula unit, or about 1/2 carrier per Cu atom. Assigning a free electron value to the mass, the corresponding Fermi velocity is 0.7×10^8 m/s and the corresponding lifetime τ is 4×10^{15} s. The corresponding scattering rate $\hbar/\tau$ is ~ 0.15 eV or about $2\pi k_B T$ at 300 K. In electron-phonon systems,[24] the scattering rate corresponds to $2\pi\lambda k_B T$ where λ is the dimensionless electron-phonon coupling. Thus we fit the data with $\lambda \sim 1$, a number which is not

unreasonable. A value $\lambda \sim 1$ is much too low to account for a 90 K value of T_c by a pure phonon mechanism.

This argument should not be taken very seriously, however. For one thing, band theory does not give a single sheet in $YBa_2Cu_3O_7$. For another, the relevance of the band-picture is often doubted. However, recent photoemission measurements of List[25] show a Fermi edge. One ought at least to allow the possibility that the carrier mass $m*$ differs from the free electron value m. Then the corresponding argument leads to $\lambda \sim 1.0$ $(m/m*)$. If one wishes to increase λ but not to make $m*/m$ smaller than 1, then one will have difficulty understanding how the resistivity is so large and yet does not saturate.

II. Hall Effect

Most of the oxide superconductors have close relatives which are semiconductors or insulators and which can be reached from the superconducting phases by compositional variations of stoichiometry. Interest of course attaches to the interrelation between the properties of the semiconducting and superconducting phases, and Hall effect measurements provide perhaps the simplest probe with which to explore this interface. The Hall constant is by no means straightforward to interpret in general: only in the high-field limit is the meaning clear, and even then we need information as to how many bands are involved to understand the numbers. But the variation of Hall constant with a parameter such as the concentration of a constituent in a compound can be given a clean interpretation in many cases, and this is the situation in some of the high T_c oxides.

We consider first the data for La_2CuO_4. The pure material is non-metallic. The Hall coefficient[26] is large and T-dependent, roughly following the behavior of $\rho(T)$, although the mobility $\mu_H(T)$ has a broad maximum near 100 K in an antiferromagnetic sample with $T_N = 280$ K. Data for strontium-doped systems come from Shafer et al.[26] and Ong et al.[27] and they are in substantial agreement for

these measurements on polycrystalline material. It is found that each Sr atom substituted adds one hole, as might be expected from simple chemical considerations. Shafer et al.[26] show that the number of holes as determined by R_H is equal to the [Cu-O]+ concentration in the compound as determined iodometrically. This variation of hole concentration with Sr addition continues out to a composition $La_{1.85}Sr_{0.15}CuO_4$ beyond which there is an abrupt drop to an essentially unmeasurably small Hall constant (Fig.II.1). This behavior appears most cleanly in the data of Ong et al.[27] It is important to note that the oxygen stoichiometry becomes a problem for Sr > 0.20. Torrance et al.[28] have reported on this, and they have shown how to maintain the stoichiometry near $O_{4.0}$ for Sr concentrations as large as 0.40.

Band theory makes instead the following predictions. For x = 0, there is a half-filled band with one carrier per cell. If currents and Hall fields are in the ab plane of a single crystal, with $\vec{B} \parallel c$, such a system will have R_H small because of partial cancellations of hole-like and electron-like contributions. The cancellation is exact in the simplest 2D single band model. More sophisticated calculations[29] have cancellation at x $\approx$ 0.20, with R_H going smoothly from positive (hole-like) at x = 0 to negative at x $>$ 0.20. For $\vec{B} \perp$ c, R_H is predicted to be negative and fairly small. The Hall data for small x completely contradict this picture, as expected, because La_2CuO_4 is actually non-metallic.

The non-metallic behavior is attributed to electron-electron (Coulomb) correlations, and can presumably be modelled by an appropriate Hubbard Hamiltonian. For dimension D $>$ 1 and filling factor deviating from 1/2, the behavior of Hubbard models is not rigorously known. It is tempting to attribute the experimentally observed jump in R_H at x = 0.15 to a transition from a highly correlated metal with carrier density x = number of dopants to a conventional band Fermi-liquid with carrier density 1 - x. The transition is presumably driven by free-carrier screening of the repulsive Coulomb effect (Hubbard U). The difficulty is then how to relate this transition to the occurrence of superconductivity,
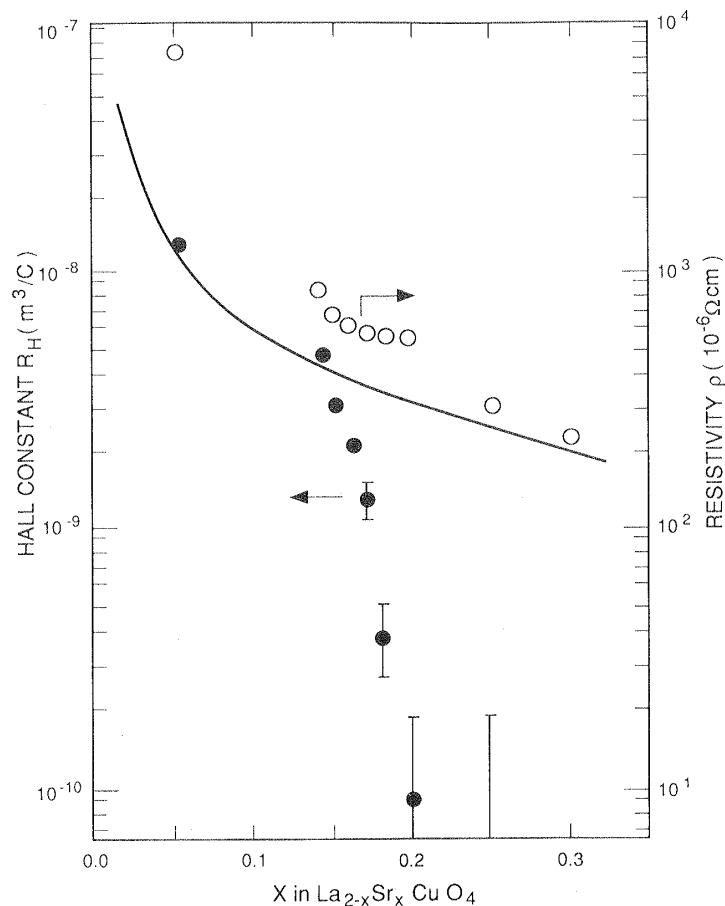
Fig. II.1 R_H and resistivity at 77 K versus Sr concentration from Ong et al. (Ref. 27).

especially since no sharp changes in superconducting properties occur at x = 0.15. Three routes are available; all invoke sample inhomogeneities to argue that the true intrinsic change in R_H of a homogeneous sample would occur in a more explainable location. One route is to push the R_H jump to larger x, making the superconducting region very interesting because the normal state behavior (as seen in R_H) is not a conventional Fermi liquid. Another route is to push the R_H jump to lower x, so that the whole superconducting region is built from a conventional Fermi liquid. A third is to argue that the jump in R_H is entirely an artifact, i.e., to argue that poorly made samples are always highly correlated.

Single crystals of $La_{2-x}Sr_xCuO_4$ in the superconducting range have been hard to grow. We know of only one report[3] of R_H on such a single crystal, a thin film with x ≈ 0.06 and T_c ~ 18 ± 2 K. Only one tensor component R_{xyz} (Hall field in x or a direction, current in y or b direction, B field in z or c direction) was measured. The resulting "carrier density," $1/eR_{xyz}$ is shown in Fig II.2. At T ~ 50-100 K, their value of n corresponds to R_H ~ 1.4 x 10 9 m3/C, a fairly low value, smaller by a factor of ~6 than the interpolated value at x = 0.06 in Fig II.1, and larger by a factor of ~3.5 than the band theory prediction.[29] Perhaps the most interesting aspect of Fig II.2 is that $1/R_H$ is seen to have a strong linear T-dependance A + BT above 150 K. The room temperature value of R_H is even smaller, farther from the ceramic data of Fig II.1 and closer to band theory (the discrepancy of 2.4 then lies within the expected accuracy of the available solution of the Boltzmann equation[29]). However, band theory cannot easily account for the T-dependence, and the phenomenon is seen even more strikingly in $YBa_2Cu_3O_7$.

Behavior somewhat analogous to that seen in Sr doped La_2CuO_4 is found in $YBa_2Cu_3O_{7-x}$ as x is varied (Fig.II.3). The oxygen stoichiometry corresponding formally to pure divalent Cu is 6.5 (x = 0.5). This is exactly the region below which semiconducting behavior sets in and where we see in the polycrystalline sample a Hall constant R_H with a rapid variation in nominal hole concentration[30] $1/R_H$. For x < 0.5, there is a long plateau region of R_H which
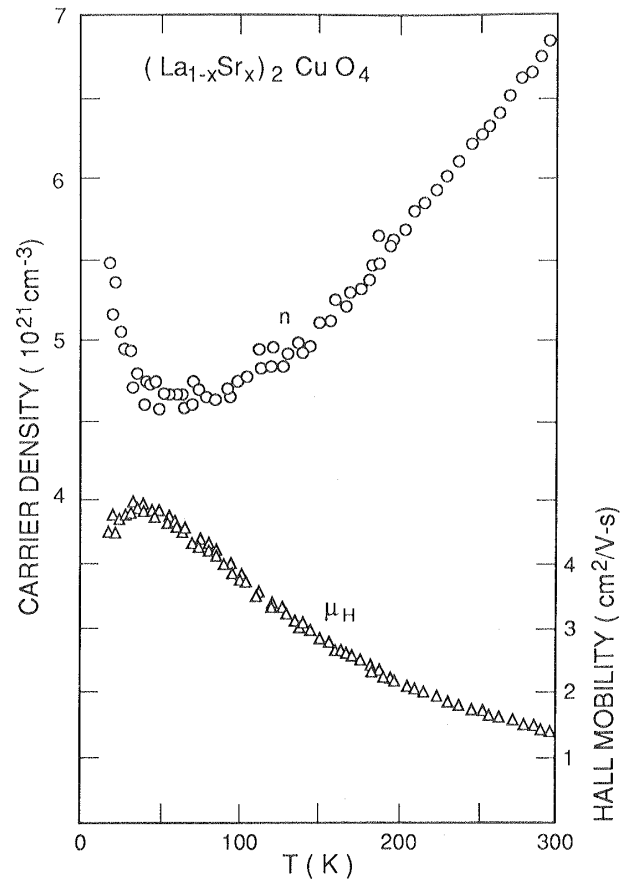
Fig. II.2   Carrier density ($1/R_H e$) and Hall mobility for a single crystal thin film B $\parallel$c (Ref. 3).
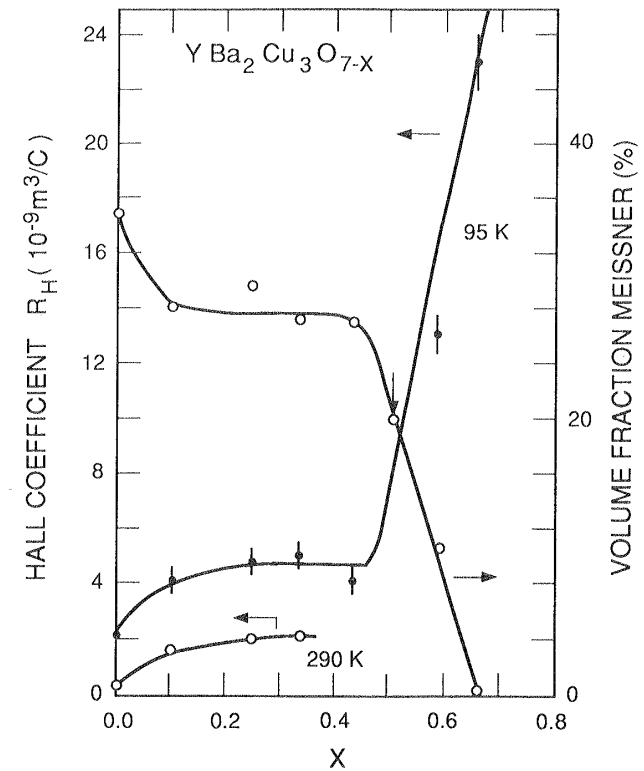
Fig. II.3 R_H versus x for $YBa_2Cu_3O_7$ from Wang *et al.* (Ref. 30). The superconducting volume fraction is also shown.

corresponds to 0.24 holes/planar Cu, close to the value found for the Sr doped La_2CuO_4 40 K superconductor. The plateau in R_H corresponds to the plateau in T_c vs. x at 55 K. For x = 0, R_H is roughly 40% smaller than in the plateau region, and it is here that T_c is 90 K.

Thus, T_c correlates nicely with $1/R_H$ or with minimum carrier density. The most unusual feature is a strong temperature dependence

$1/R_H \sim A + BT$. Unlike $La_{2-x}Sr_xCuO_4$ (Fig. II.2), $YBa_2Cu_3O_7$ has the coefficient A close to zero. There is no generally accepted explanation.

Single-crystal data are available from several laboratories. An example from Penney et al.[31] is given in Fig. II.4. When $\vec{B}$ is $\parallel c$ (so that electron orbits are in the metallic ab plane) the sign is positive (hole-like) and $1/R_H$ goes accurately like T. When $\vec{B}$ is $\perp c$, the sign is negative, and the T-variation is weak. The signs and orders of magnitude agree with the predictions of band theory,[32] but

Fig. II.4 $V_o/|R_H|e$ for a single crystal of $YBa_2Cu_3O_7$ (Ref. 31).
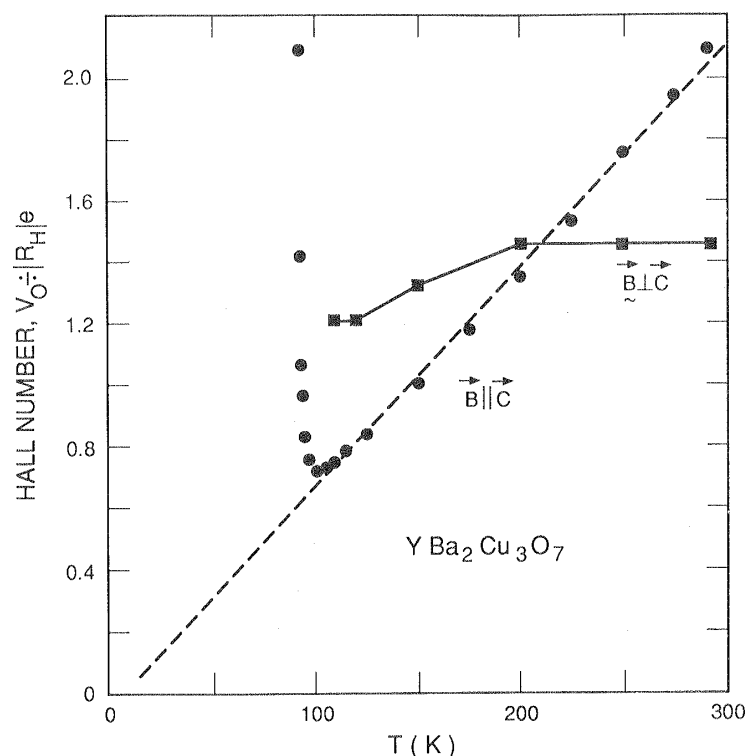$V_o = 175 \; \text{Å}^3$ is the volume per formula unit.

band theory gives only a weak T-dependence. Forro et al.[33] report a similar experimental value of R_H with $\vec{B} \perp c$ at room temperature, but find a significant T-dependence in the opposite direction($|R_H|$ decreases as T decreases). Their data with $\vec{B} \parallel c$ are smaller than those of Penney[31] but have a similar T-dependence. Stormer et al.,[5] looking at epitaxial thin films of $YBa_2Cu_3O_7$ grown on $SrTiO_3$ (100), found both the magnitude and T-dependence of R_H to vary significantly with sample. Of six samples, only one (which had the highest critical current density) showed $1/R_H \sim BT$, three of the samples had somewhat similar T-dependence, and two had R_H smaller and weakly T-dependent.

The Hall constant has also been reported for a single crystal sample of the Bi-based cuprates,[34] and again hole-type conduction is found in the plane. In the case of the lower T_c $BaBiO_3$-based superconductors, measurements on $BaPb_{0.7}Bi_{0.3}O_3$[35] show a strong temperature variation of R_H which has been interpreted as arising from the sum of activated- and temperature-independent terms, the former depending on the concentration of O-vacancies in the films. In this way it has been argued that most of the temperature dependence of the electrical resistivity arises from the temperature dependence of the carrier concentration in this material.

III. Thermopower

Relatively little has been reported concerning the thermopower of the high T_c oxides. This is presumably due in part to the fact that a simple interpretation of the data is generally difficult, the thermopower involving as it does the derivative of the density of states at the Fermi level. The measurements have the advantage that they are fairly simple and make only modest demands on sample geometry. One also determines the sign of the dominant carriers in the material.

Most of the data we are familar with are on $YBa_2Cu_3O_7$. Single crystal data of Wang and Ong[36] find that the thermopower is positive both in and out of plane. The anisotropy is considerably less than

reported for the resistivity, and the temperature dependence is strong perpendicular to the Cu-O planes (Fig. III.1). There is a peak in the in-plane thermopower at T_c. The in-plane thermopower found by Howson et al.[37] is negative, but also peaks at T_c. A study by Yu et al.[38] agrees with this last result. These authors also looked at the magnetic field dependence above T_c for $La_{1.85}Sr_{0.15}CuO_4$ at fields up to 30 T and found no effect. Their hope to freeze out the spin entropy contribution seems unrealistic in view of the large exchange coupling that two-magnon Raman[39] experiments appear to find. Kwok et al.[40] have reported the variation and temperature dependence of the thermopower of $YBa_2Cu_3O_x$ for $6 < x < 7$. The temperature dependence changes markedly in the vicinity of $x = 6.5$, but the metallic-like behavior for $6.1 < x < 6.5$ remains unexplained.
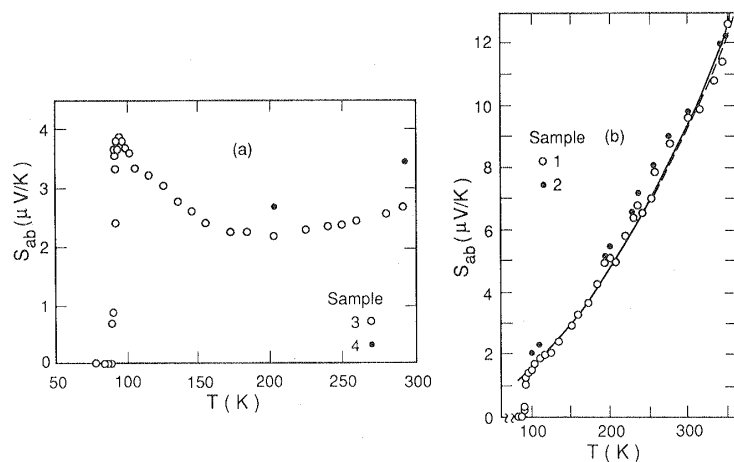

Fig. III.1 S(T) for YBa_2Cu_3O from Wang and Ong (Ref. 36).

IV. Magnetic Properties

The nature of the underlying pairing mechanism is the primary question concerning high T_c oxide superconductivity. While there is still a slight possibility for a phonon mechanism, most theorists have looked to exciton and magnetic interactions, or their combination. Considerable experimental attention has focussed on the striking magnetic properties of the cuprates. There appears to be no magnetism in the $BaBiO_3$ based superconductors, and so we must conclude that either there is more than one mechanism for high T_c in the oxides, or that the cuprate magnetism has nothing to do with superconductivity. But the magnetic behavior of the cuprates is interesting in its own right, and studies of these materials are providing new arenas for the study of correlated-electron systems.

We begin with the properties of La_2CuO_4. The first point to make concerns the stoichiometry of the compound. There were early reports that large variations in La stoichiometry below 2 and oxygen stoichiometry below 4 were possible, but neutron line profile analysis now shows that La and Cu stoichiometries are within 1 atomic % of their nominal ones. However, single crystals grown from PbO fluxes were found to contain approximately 2 atomic % Pb incorporated into the crystals.[41] Similarly, crystals grown from fluxes based on $Li_4B_2O_5$ appear to incorporate Li at similar levels.[42] A number of the properties of La_2CuO_4 are now known to be quite sensitive to substitutions of this sort, and it is necessary to characterize samples whose properties are under investigation.

The oxygen stoichiometry problem is more controversial. The usual practice has been to write the formula as La_2CuO_{4-y} which carries the implicit assumption that the oxygen stoichiometry never exceeds 4. Below we shall present arguments which suggest that the stoichiometry of oxygen is always on the high side, the lower bound of four occurring when Cu has a formal valence of +2 in the compound. So within the error of neutron determination of the La and Cu stoichiometries, we will argue that the formula is more appropriately written La_2CuO_{4+y}. Firstly, high pressure oxygen loading

experiments[43] have shown that the material can be prepared with y = 0.13 in a slightly different structure. Furthermore, it is known from magnetic studies of the related compound La_2NiO_4 that the 3-dimensional magnetic ordering temperature is rapidly suppressed[44] when the oxygen stoichiometry deviates from 4, presumably due to the frustrated character of the magnetic ordering and the attendant defect sensitivity. In La_2CuO_4, inert gas or vacuum annealing is found[45] to raise the Neel temperature T_N substantially, again consistent with the view that the procedure is approaching oxygen stoichiometry 4.0 from above. And we have the result that the Hall constant is positive for nominal La_2CuO_4, consistent with a small excess of oxygen above 4.0. Where this oxygen sits in the lattice is not yet known, and it is interesting that the other rare earth cuprates R_2CuO_4,[46] all of which form in a related but different structure, are n-type and cannot be made metallic via chemical substitutions.

Single crystals of La_2CuO_4 can be grown from excess CuO and these appear to be within 1 atomic % of having full La and Cu occupancy. The magnetic susceptibility of these crystals is quite anisotropic[47] (Fig. IV.1): the basal plane susceptibility is roughly half that perpendicular to it. There is a peak in the susceptibility near room temperature, and neutron diffraction[48] has shown this peak to correspond to the 3D ordering shown in Fig. IV.2. In the planes the spin arrangement k-vector is consistent both with what would be expected from the nested aspect of the band-structure-predicted Fermi surface and from a strongly coupled 2D Heisenberg antiferromagnet. As mentioned above, the tetragonal K_2NiF_4 structure has an intrinsically frustrated face-centered lattice of Ni's; the slight orthorhombic distortion present in the La_2CuO_4 structure lifts this frustration slightly, and the 3D magnetic structure chooses an interlayer arrangement with antiparallel spins on the nearest interlayer sites. The Neel temperature depends strongly on annealing protocol.[45] T_N is generally observed in the range 240-280 K, but careful inert-gas annealing has raised T_N to 308 K,[45] and a vacuum anneal, which decomposes part of the surface of a crystal, raises T_N to 326 K.[45]
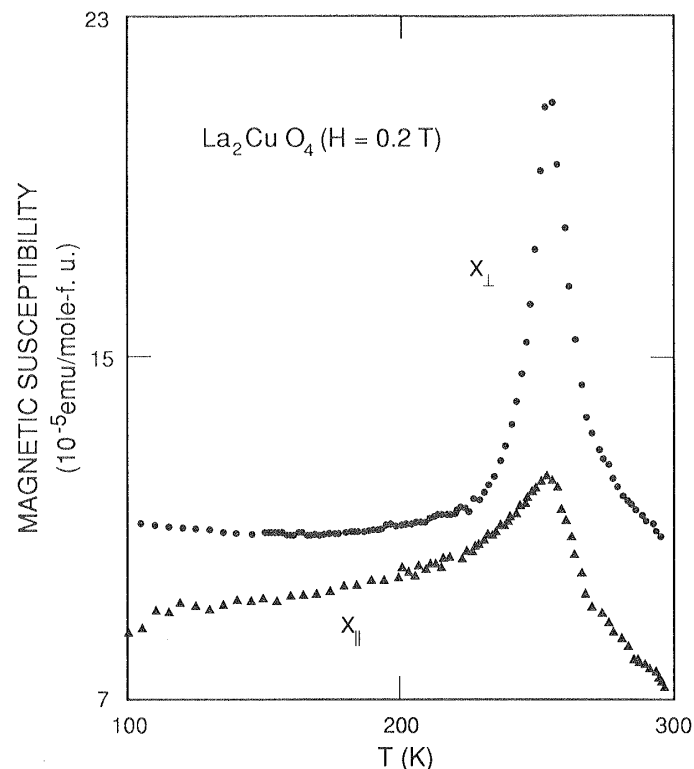
Fig. IV.1   Anisotropy of χ in La_2CuO_4 (Ref 47).

The chapter on neutron scattering results covers in detail the microscopic magnetic properties of La_2CuO_4, so our discussion will be restricted mainly to macroscopic aspects of the magnetism of the cuprates. However, we note one important result of the neutron work here. This is that there are extremely strong 2D fluctuations in the Cu-O planes, characterized by a temperature of order 1000 K.[49] These fluctuations have also been seen in two-magnon Raman scattering.[39]

Fig. IV.2   3-D Ordering in La_2CuO_4 (Ref. 48)

These large interactions account for the rather flat temperature dependence of the magnetic susceptibility, excepting the region very near T_N.

Applied fields induce a weakly ferromagnetic phase below T_N. This was first detected by Cheong et al.[50] in a PbO-flux grown crystal, which NQR[51] measurements found to be only partially ordered magnetically, apparently from incorporated Pb in the crystal. Subsequent neutron work[52] found that 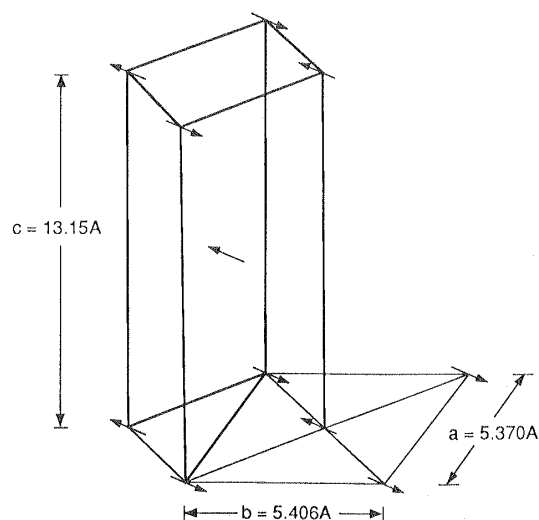this field-induced weak ferromagnetism arose from the preference of the Cu spins to lie in the plane of its orthorhombically tilted (and elongated) CuO_6 octahedron. This gives rise to a small net resultant moment from two neighboring, antiferromagnetically aligned spins, but each of these resultant moments is opposed by another anti-aligned resultant moment

in the crystal. The applied external field flips this opposed resultant moment. We show magnetization data for this transition[53] in Fig. IV.3. Included in the figure is the H-T phase diagram determined by Cheong[55] which indicates that the transition field goes discontinuously from zero to finite values at T_N. It has also been found that there are large resistance effects at T_N, especially perpendicular to the Cu-O planes, provided there are sufficient carriers present (Fig. IV.4). Crystals with very low conductivity show no conductivity anomaly at T_N.

The effect of Sr doping is to depress T_N rapidly, and for x > 0.02 no long-range magnetic order is found. There has been some suggestion that a spin-glass phase exists for 0.02 < x < 0.15 but this is not certain.[54] This muon experiment on Sr doped samples indicates that the Cu moment maintains its full value in this range of x in spite of the lack of long-range order. The superconducting phase diagram[11] for Sr-doped La_2CuO_4 is shown in Fig. IV.5. Antiferromagnetic order appears not to coexist with the superconducting phase.

Two kinds of magnetic order have been found in the materials related to $YBa_2Cu_3O_y$. The first is found in the materials containing rare earth elements carrying localized f-moments.[55] These f-moments
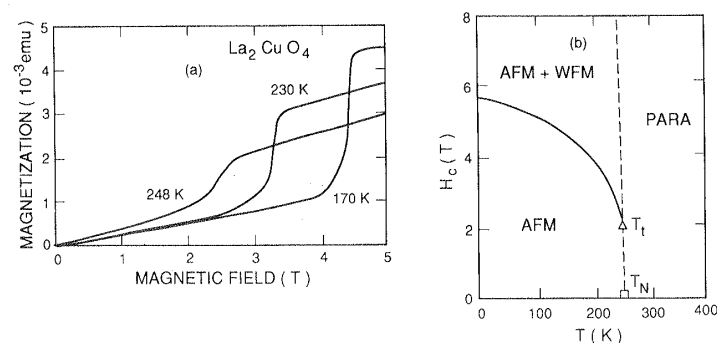

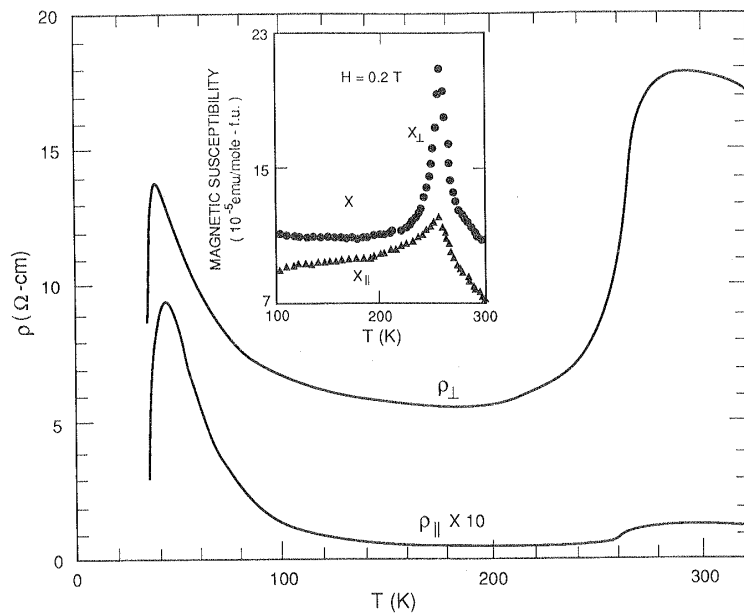Fig. IV.3   a) M versus H and b) H-T phase diagram (Ref. 53).

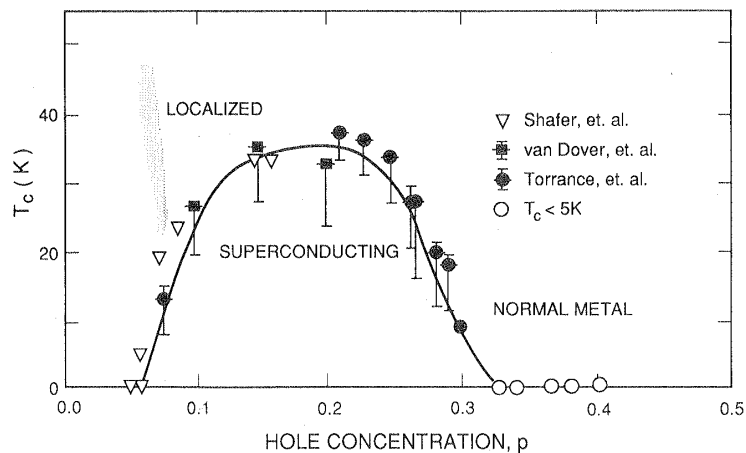Fig. IV.4 ρ versus T near T_N (Ref. 53).

Fig. IV.5 Sr doped La_2CuO_4 phase diagram (Ref. 11).

order at low temperatures, and the ordering coexists with superconductivity. For samples of the 123-materials with y < 6.5, this ordering still occurs unchanged. There appears to be no depression of the superconducting T_c by these f-moments, and the above facts show that the rare earth magnetism is essentially independent from the high T_c oxide superconductivity. We give in Table IV.1 data pertinent to the rare earth ordering in the 123-materials.

Table IV.I Néel Temperatures of $RBa_2Cu_3O_{7-x}$

	$T_N(K)$	Ref.
Pr	< 0.5	56
Nd	< 0.5	56
Sm	0.60	56
Eu	0	
Gd	2.1	55
Tb	*	
Dy	0.95	57
Ho	0.17	57
Er	0.59	57
Tm	*	
Yb	*	

*not reported

The second kind of magnetic ordering observed[58] is ordering of Cu moments in the semiconducting 123-materials with y < 6.5. This magnetic ordering does not, therefore, coexist with the superconductivity. To date, the Cu-moment ordering has been studied in Y, Nd and Er 123-materials. All these compounds show T_N near 500 K for y = 6.0. T_N decreases smoothly to 0 K as y → 6.5. Only the Cu's in the planes carry a moment at high T, and these are aligned antiferromagnetically along the direction perpendicular to the planes. It has also been observed in some samples that a second

magnetic phase grows in and replaces the above mentioned phase at low temperature. For a Nd sample with y = 6.1, this second phase started growing in below 90 K.[59] The strange feature of this transition is that all the Cu's now carry moment, a chemically important fact indicating that, at least in these O-deficient materials, both chain and plane Cu-sites have similar oxidation states. This low temperature phase has the spins lying parallel to the Cu-O planes. It remains to be determined what conditions lead to this second ordering and how general it is.

The question of interest of course is whether or not some of these magnetic interactions survive in the materials which become superconducting. There are at present only tentative results on this question. A neutron measurement on Sr-doped La_2CuO_4[60] indicates that the magnetic interactions are there in force in the superconducting material, but some questions remain to be cleared up concerning the sample on which the measurements were made, principally concerning sample homogeneity. The two-magnon mode has been reported in Y 123-material, broadened but at the same energy.[61] The question here is whether or not the surface layer measured is truly indicative of the bulk. Photoemission experiments,[25] have found that oxygen is immediately lost from freshly cleaved surfaces that are not maintained near He temperature.

V. Elastic Properties and Ultrasound

Elastic properties of the high T_c superconductors and related compounds have been measured on superconducting and non-superconducting ceramics at high temperatures (above 4 K), on superconducting ceramics at very low temperatures (1 K and below), on large (2.5 mm) and superconducting single crystals for which the Meissner effect has not been measured, and on non-superconducting single crystals. In the normal state, two points immediately attract attention to the importance of the elastic constants. They are the intrinsic anisotropy of the high-temperature superconductors, and the

possibility of using elastic-constant data in the high temperature, phonon-dominated regime to sort out the specific heat. Unfortunately, the most difficult measurements to interpret are those performed at high temperatures on ceramics, where no anisotropy information is available. The root of the difficulty may be inferred from the work of Blendell et al.[62] where ultrasound determinations of the elastic constants of sintered $YBa_2Cu_3O_y$ superconductors of various densities were corrected for porosity using the expressions of Ledbetter and Datta.[63] Their uncorrected results are shown in Table V.I, where B is the bulk modulus, E is Young's modulus, μ is the shear modulus and σ is Poisson's ratio.

Table V.I

Porosity	v_ℓ(km/s)	v_s(km/s)	σ	E(Gpa)	B(Gpa)	μ(Gpa)	ρ(gm/cc)
12.9%	4.87	2.76	.264	107	75.5	42.4	5.56
32.6%	3.63	2.06	.263	46.1	32.4	18.3	4.30

As shown, they find that for their sample, with a porosity of 12.9% (theoretical density from x-rays is 6.383 gm/cc) the longitudinal sound velocity v_ℓ was 4.7 km/s and the transverse wave velocity v_s was 2.76 km/s. For their lower-density sample, having 32.6% porosity, v_ℓ = 3.63 km/s and v_s = 2.06 km/s. Upon correcting for porosity, the higher-density sample extrapolated to v_ℓ = 5.22km/s and v_s = 2.92km/s, while the lower density sample extrapolated to v_ℓ = 4.32km/s and v_s = 2.35 km/s. Furthermore, the predicted value (corrected for porosity in the denser sample) of the bulk modulus was 1.39 x 10^{12} dynes/cm^2, an extremely low value compared to values for a single superconducting[64] crystal of $YBa_2Cu_3O_y$ measured in the b direction (long axis of the orthorhomb) of about 1.5 x 10^{12} dynes/cm^2. Thus one must conclude that intrinsic structural differences exist between samples of differing densities. This is not surprising, as at all the frequencies for which such quantities have been measured, the wavelength of sound is much larger than the grain size. One probes,

therefore, the properties of the bonds between grains as well as the intrinsic properties. These structural differences, associated perhaps with sample variations, heat treatment, and oxygen content, can cloud any conclusions based on ceramic measurements. This is illustrated further in $YBa_2Cu_3O_y$ superconductors by the observations of Kim et al.,[65] who find that v_ℓ varies from 4.7 km/s for $y = 6.2$, $\rho = 6.12$ gm/cc to 3.95 km/s, $\rho = 6.37$ gm/cc for $y = 6.8$, opposite in density dependence to the results of Blendell, but with no obvious fundamental processing differences except for oxygen anneal. More confusion exists in the interpretation of the temperature dependence of v_ℓ for the purpose of understanding the superconductivity. It increases on cooling, as measured by Ewert et al.[67] in $YBa_2Cu_3O_y$ ceramic, shown in Fig. V.1 but decreases on
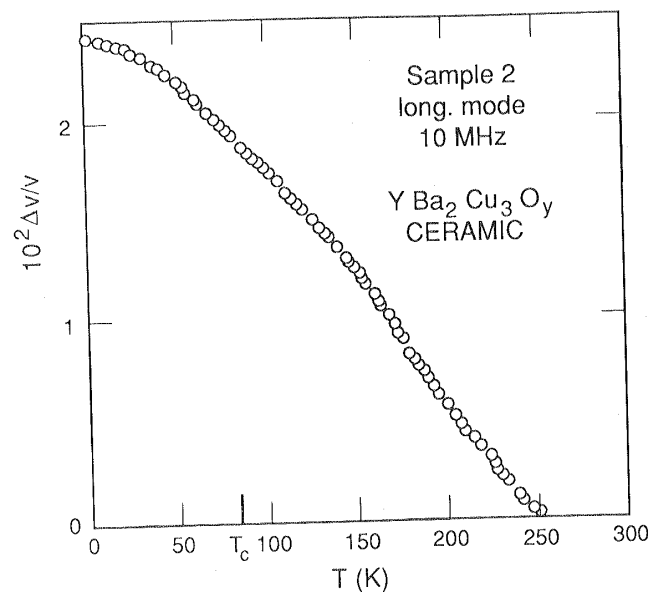
cooling in ceramic $La_{1.85}Ba_{0.15}CuO_4$, as shown in Fig. V.2.[67] Nevertheless, one may estimate the phonon specific heat and the Debye temperature from the Debye-average sound velocity which is

$$v_D = \left[\frac{1}{3} \left[\frac{1}{v_\ell^3} + \frac{2}{v_s^3} \right] \right]^{-1/3} \qquad (1)$$

We find $v_D = 3.25$ km/s if we use the corrected data of Blendell et al. on their higher-density $YBa_2Cu_3O_y$ sample. The Debye temperature is then a little over 280 K if we use the theoretical density. This is to be compared with a Debye temperature of 392 K[69] determined via specific heat for a superconducting single crystal with a T_c of 89 K. The single-crystal elastic data are consistent with specific heat data obtained on ceramics,[69] where values nearer to 360 K are observed. Thus the discrepancy, though suggestive of porosity and ceramic structure effects, is certainly real because it

Fig. V.1 v_ℓ for $YBa_2Cu_3O_y$ ceramic from S. Ewert et al. showing a normal increase in v_ℓ cooling below 300 K (Ref. 66).
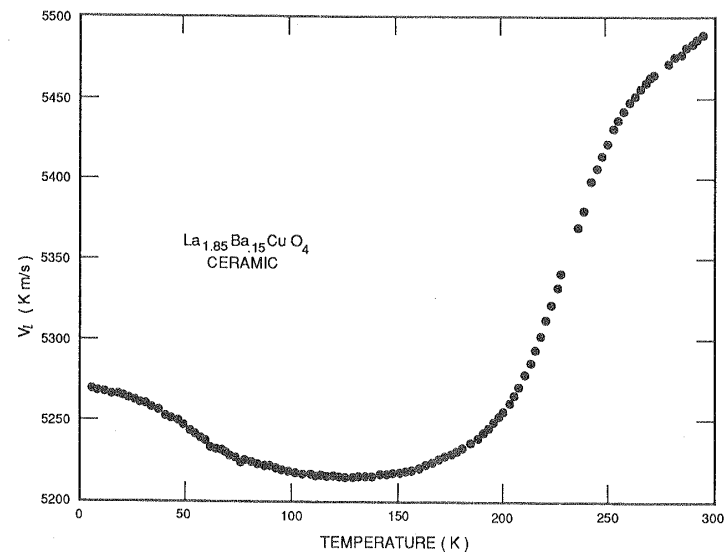

Fig. V.2 v_ℓ for a single-crystal $La_{1.85}Ba_{0.15}CuO_4$ ceramic showing the decrease in sound velocity on cooling below 300 K. From K. Fossheim et al. (Ref. 67).

is hard to imagine how this compound could have a v_ℓ of 7.3 km/s and a v_s of 4.1 km/s, the values predicted by the specific heat data if we use $\sigma = 0.26$. A highly anisotropic structure could, however, limit the specific heat contribution from the acoustic-branch phonons.

The superconducting phase transition generates a discontinuity in compressional elastic constants which can be obtained from a thermo-dynamical treatment. Observation of such effects are relevant to the interpretation of normal-state properties because the discontinuity, Δv_ℓ in the bulk sound velocity of an isotropic superconductor, given by

$$\Delta v_\ell = - \frac{v_\ell \Delta C}{2T_c}\left[\frac{dT_c}{dP}\right]2 \qquad (2)$$

where ΔC is the discontinuity in specific heat at T_c and v_ℓ is the bulk sound speed, is a measure of the required resolution for ultrasound measurements to shed light on the free energy changes associated with superconductivity. Saint-Paul et al.[64] find no anomaly at T_c in their superconducting single crystal (nor could they measure the anisotropies in the sound velocities) within the resolution of their measurement, which is insufficient to resolve the expected drop (Fig. V.3). Neither do they find any change in slope of the sound velocity at T_c in contrast to observations on ceramics by, for example Bishop et al.[70] shown in Fig. V.4. Thus, even though Saint-Paul's single crystal was probably too large to be properly oxygenated, it is unlikely that hysteretic effects or anomalous changes in v_ℓ or its slope are important to superconductivity. They are most likely manifestations of the ceramic nature of the samples. Even in such high-quality glasses as fused silica, the sound velocity decreases on cooling from 300 K and the ultrasonic attenuation increases[71] to peak at 40 K. In the high T_c superconductors, attempts have been made to measure the discontinuity in value or in slope of the shear elastic constants expected at T_c. Again, the properties of the ceramics intrude. The difficulty with shear in ceramics is well discussed by Pippard.[72] Based on his arguments and
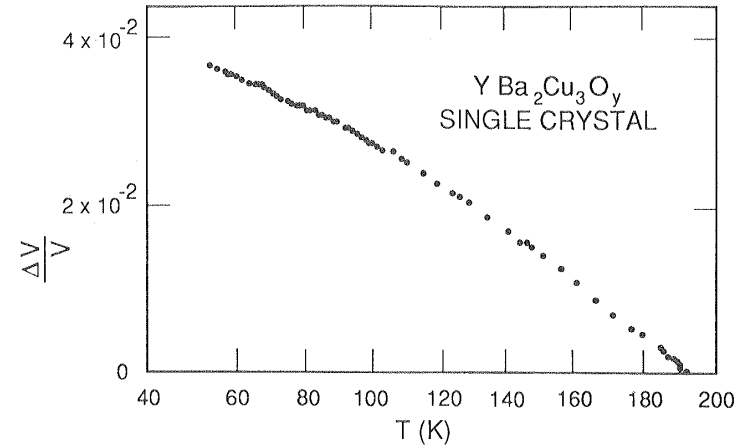
Fig. V.3 v_ℓ for a single-crystal $YBa_2Cu_3O_y$ with a T_c of about 90 K but with no determination of the Meissner fraction. Note the smooth, monotonic increase in sound speed on cooling. The measurement was of insufficient precision to detect discontinuities at T_c. From M. Saint Paul et al. (Ref. 64).

reasonable estimates[73] for the pressure dependence of the thermo-dynamic critical field, we find that the expected discontinuities are of the order of 100 ppm for the value of the bulk modulus, and, absent the unlikely possibility of spontaneous shear occurring at T_c, 0 for the shear modulus; changes in slope are also small. Thus, the very large effects in the slope of the shear modulus such as those observed by Ledbetter[74] or Bhattacharya[75] would overwhelm the small thermodynamically-induced break in slope at T_c at a temperature only 1 K away from T_c. The implications are obvious. It is interesting to note that only the high-resolution data of Brown et al.[73] on the shift in bulk modulus at T_c in $GdBa_2Cu_3O_y$ (Fig. V.5) provide thermodynamic agreement, required by Eq. (2), with the specific

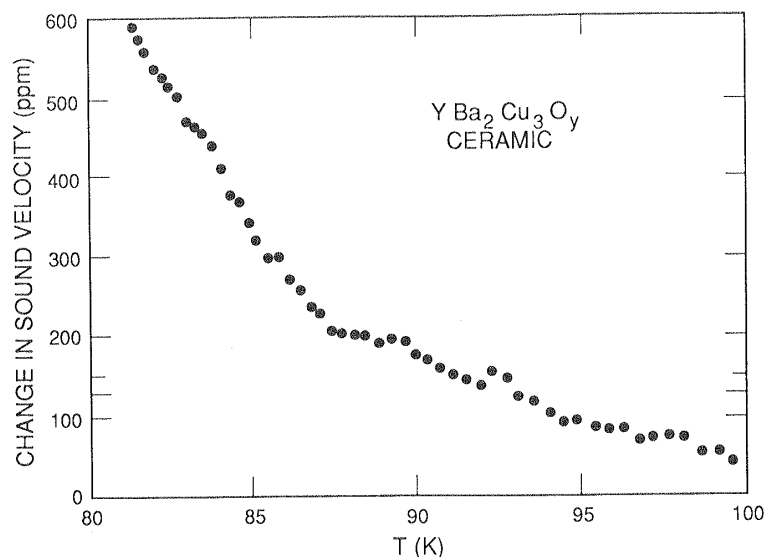Fig. V.4 v_ℓ for a ceramic superconducting sample of $YBa_2Cu_3O_y$ showing a break in slope at T_c which is not seen in the ceramic. From Bishop et al. (Ref. 70).

heat data of M. E. Reeves *et al.*[76] and the pressure dependence of T_c measured by Borges *et al.*[77] Brown, however, had to cycle his pressed pellet up and down in temperature for many days before the small "earthquakes" finally subsided to the point where a 70 ppm discontinuity was unmasked. This low-level relaxation of ceramic pellets would certainly bring into question the extremely noisy x-ray data of Horn *et al.*[78] where a discontinuity in the difference between the two in-plane lattice constants at T_c was claimed. On the basis of the same thermodynamic arguments which obtain discontinuities in specific heat, thermal expansion, and elastic constants at T_c, one finds that for the isotropic case, no discontinuity in volume is expected. Based on similar reasoning, but including the fully
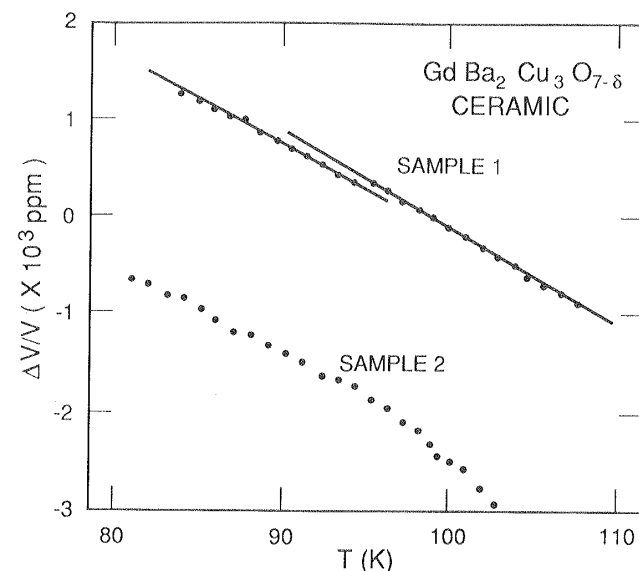
Fig. V.5 v_ℓ for a ceramic superconducting sample of $GdBa_2Cu_3O_y$. Shown are the first cool-down for sample II and data for sample I after many thermal cycles, which served to reduce random discontinuous jumps below the level of the expected discontinuity (shown) at T_c. From S. E. Brown *et al.* (Ref. 73).

anisotropic stress tensor, it is only by a coincidental effect that the difference between two lattice constants could be discontinuous for an orthorhombic solid.[72]

   The pressure dependence of elastic constants has also been studied by using x-rays. In $La_{1.7}Ba_{0.3}CuO_{4-y}$, Moret[79] finds an anomaly in the a-axis (short axis) compressibility: the a-axis does not change up to 7 kbar, while the c-axis compresses uniformly. Above 7 kbar, they find $da/adp = 2 \times 10^{-4}/kbar$ and $dc/cdp = 1.7 \times 10^{-4}/kbar$. A similar anomaly is observed by Shelton[80] in $La_{1.85}Ca_{0.15}CuO_4$.

However, neither Terada nor Takahashi[81] see such effects in either
$La_{1.8}Sr_{0.2}CuO_{4-y}$ or $La_{1.4}Sr_{0.6}CuO_{4-y}$ where compressibilities of both
lattice constants in the former are $2.5 \pm 0.4 \times 10^{-4}$/kbar and
$da/adp = 1.9 \times 10^{-4}$/kbar and $dc/cdp = 2.24 \times 10^{-4}$/kbar for the
latter. Thus the basal plane is perhaps stiffer than the direction
normal to the planes, but perhaps not by as much as the error bars on
the anisotropy which are about 20%.

At very low temperatures, one might expect many of the anomalous
results arising from the problems with ceramics to disappear because
the thermal expansion coefficients, related to the Debye temperatures
of hundreds of degrees,[68] freeze out. In ultrasound measurements on
$YBa_2Cu_3O_y$ from 10 K to 5 mK, Golding et al.[82] postulate a
sufficiently high density of tunneling states (on "two-level
systems") to fully account for the linear term observed in the
specific heat[76] with a quasi-particle density as low as it would be
in a fully gapped superconductor. Golding attributes the tunneling
states to mobile oxygen defects.

VI. Thermal Conductivity

Although the thermal conductivity is a useful tool in studying
superconductors, the data available for the high T_c superconductors
above T_c is sparse. Because all the measurements we know of above
10 K have been performed on ceramics, the usual precautions must be
taken in drawing conclusions. The data of Uher et al.[83] (Fig. VI.1)
on $YBa_2Cu_3O_y$ ($T_c = 92$ K) is typical. Above T_c, the thermal
conductivity increases from about 3.5W/mK at T_c to about 4W/mK at
300 K. From these values and their resistivity data on the same
specimen, they estimate that at least 90% of the thermal conductivity
comes from phonons. This large phonon background effectively masks
any features in the electronic thermal conductivity. Below T_c Uher
and others[84] see an increase in thermal conductivity. This is
opposite the effect seen in classical superconductors, in which
electronic part dominates and freezes out exponentially as the gap
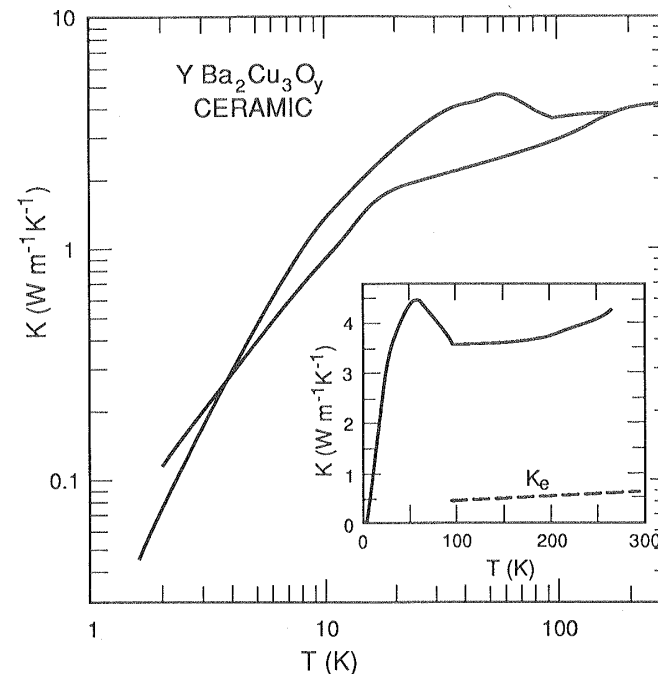
Fig. VI.1   The thermal conductivity of $YBa_2Cu_3O_y$ ceramic showing the
increase below T_c. From C. Uher et al. (Ref. 83).

develops. For the high T_c materials, it appears that the decrease in
electron-phonon scattering below T_c is more important than the
freezing out of electrons. Bayot[84] concludes that this is evidence
for strong electron-phonon coupling, but Uher warns that both strong
and weak-coupling classical superconductors with low electronic
thermal conductivity in the normal state also display this
behavior.[85][86] At very low temperatures (0.1-7 K), the thermal
conductivity remains small and is similar to that observed in other
sintered ceramics.[87] These data[87] overlap those of Bayot[84]
and, within a factor of two, agree with them.

VII. Electrodynamics

Measurements of the electrical conductivity of the high T_c materials in the normal state have been made at infrared frequencies and at dc. Intermediate frequency measurements of the complex conductivity are not possible because the $\rho\epsilon$ (where ρ is the resistivity and ϵ is the dielectric constant) time constant is too small in a metal. However two sets of measurements in the microwave regime (1 GHz to 100 GHz) have been made on single crystals of Eu_2CuO_4 and La_2CuO_4.[88][89] These materials are semiconductors with a 1.7 eV gap. In both materials at frequencies near 10 GHz a large resonant response is observed. Such a mode indicates collective transport, in this case with a large effective mass of many 10's of electron masses, which is the result of a highly correlated ground state. The spectral weight of the mode in the Eu compound, shown in Fig. VII.1, is activated (with an activation energy of 630 K) and is strong enough to produce a dc dielectric constant of about 1000 at 300 K. The material had a Hall carrier density which is activated[90] (activation energy of 700 K) in agreement with the activation energy of the spectral weight. Such an activated spectral weight is unlike that of a charge density wave (which is IR active at temperatures below T_c, much like the behavior of a superconductor). The La_2CuO_4 displays a similar mode, but with a more complicated temperature dependence: the static dielectric constant remains high (about 70) when extrapolated to zero temperature. This value of dielectric constant is typical of perovskites, but the collective mode is not. This mode, because of its close coupling to the dc carrier concentration, indicates that some very complicated phenomena may accompany current transport in the semiconducting copper oxides.
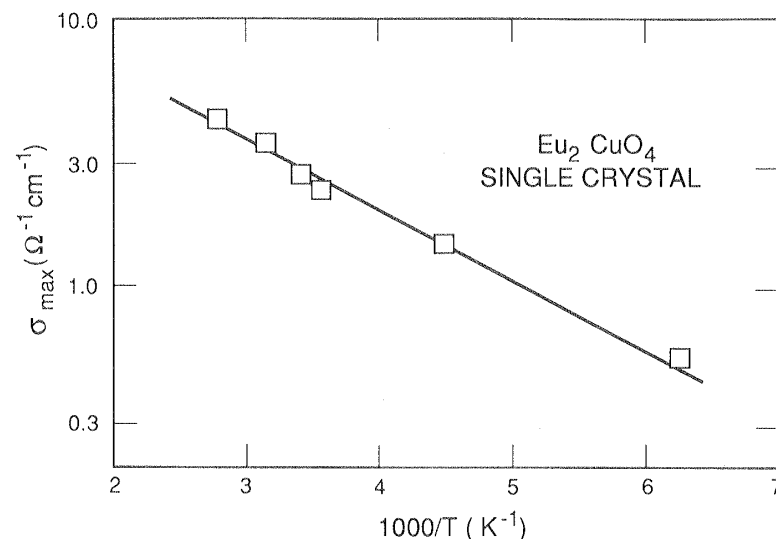

Fig. VII.1   The peak conductivity at 12 GHz of the microwave collective mode versus temperature for a single crystal of Eu_2CuO_4 showing the freezing out of the mode on cooling, from Ref. 88.

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