

Hall effect of the high- T_c superconducting oxides Bi-Ca-Sr-Cu-O and $Tl_2Ca_2Ba_2Cu_3O_x$

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The Hall coefficient R_H has been measured in ceramic samples of the high- T_c superconductors Bi-Ca-Sr-Cu-O and $Tl_2Ca_2Ba_2Cu_3O_x$. The Bi compound is a mixture of the 2:1:2:2 and 2:2:2:3 phases whereas the Tl compound is single-phase 2:2:2:3. In both systems, R_H is T dependent and positive. A $1/T$ dependence is observed in the Bi compound. We discuss the significance of the low Hall number $1/R_{He}$ (equivalent to ~ 0.1 holes per Cu ion near T_c) implied by the large R_H observed in both systems.

High-temperature superconductivity has been observed in two new families of compounds based on Bi-Ca-Sr-Cu-O (Ref. 1) and on Tl-Ca-Ba-Cu-O (Ref. 2). Structural analyses³⁻⁶ of both families show that they are based on CuO_2 planes as in the earlier systems based on La_2CuO_4 (2:1:4) and $YBa_2Cu_3O_7$ (1:2:3). A novel feature of both the Bi and Tl compounds is the occurrence^{7,8} of a series of distinct compounds in which the number of consecutive CuO_2 layers N varies from 1 to 3. In the Tl system, for example, the compounds 2:0:2:1, 2:1:2:2, and 2:2:2:3 (where the numbers refer to the stoichiometry of Tl, Ca, Ba, and Cu, respectively) correspond to $N=1, 2,$ and 3 . There appears to be a firm correlation⁹ between the observed transition temperature T_c and N in both systems. This has been interpreted in terms of an increase in the density of states within the context of conventional BCS pairing theory,¹⁰ or as evidence for the dominant importance of the interplane coupling energy.¹¹

Earlier work on the 2:1:4 system has shown a definite correlation between T_c and the concentration x of Sr dopants (up to $x=0.15$) (Refs. 12 and 13). The situation in 1:2:3 is more complicated. Oxygen doping studies on $YBa_2Cu_3O_y$ show a monotonic correlation between T_c and the observed Hall number n_H (defined as $1/R_{He}$).¹⁴ However, a linear relationship between T_c and n_H is obscured by the occurrence of the 55 K phase within the interval $6.7 < y < 6.5$ (where R_H is independent of y). The interpretation of n_H in terms of the actual carrier concentration n is also problematical because n_H varies linearly with T (Refs. 14 and 15).

Unlike $YBa_2Cu_3O_y$, there are no chains in the Bi and Tl compounds, so that ambiguities do not arise in identifying the valencies of the Cu ions in the Bi and Tl compounds. (All the Cu ions are in the planes.) Therefore, the determination of the Cu valency (and hence the carrier concentration) is expected to be more straightforward. However, the oxygen content has not been determined with any degree of certainty in either the Bi or Tl systems.

A significant question is whether the enhancement in T_c in the $N=3$ members (2:2:2:3) of the Bi and Tl families is due primarily to the close proximity of N CuO_2 planes, or is also assisted by a concomitant increase in the carrier

concentration. To help answer this question we have carried out Hall measurements in several samples of both the Bi- and Tl-based systems. Single crystals of the Tl family large enough for transport measurements are not presently available. Some Hall results on single crystal 2:1:2:2 of the Bi family have been reported.¹⁶ All our present Hall data are on ceramic sinters. Although single-crystal results are preferable, results on ceramics are still valuable to indicate trends from one compound to another. Conclusions drawn from these results and comparisons with single-crystal data are discussed below.

The $Tl_2Ca_2Ba_2Cu_3O_x$ samples were prepared by mixing appropriate amounts of Tl_2O_3 , $CaCO_3$, $BaCO_3$, and CuO thoroughly. After grinding, the powder was pressed into small pellets, fired in pure O_2 for 3 min at temperatures between 890 and 920°C, and then furnace-cooled. Extreme caution was taken in handling the samples. All of the above procedures were done in a toxic chemical glove box inside a fume hood. X-ray powder diffraction pattern showed two unidentified peaks at $2\theta=28.16^\circ$ and 43.2° , and otherwise single $Tl_2Ca_2Ba_2Cu_3O_x$ phase with lattice constants $a=b=3.85$ Å, $c=36.0$ Å. The Bi samples were prepared by mixing starting materials with nominal ratio of Bi:Ca:Sr:Cu = 1:1:1:2. The thoroughly mixed powder was then pressed into small pellets and fired for 100 h in air at 875°C. X-ray powder diffraction showed a very small amount of impurities of $Bi_2O_{2.75}$, and a mixture of 2:1:2:2 (40%) and 2:2:2:3 (60%) Bi-Ca-Sr-Cu-O with lattice constants $a=b=3.83$ Å, $c=30.8$ Å, and $a=b=3.83$ Å, $c=37.3$ Å, respectively.

For the two Bi samples the resistivity ρ shows a sharp drop (by 60% and 80%, respectively, in samples B1 and B2) near 110 K, followed by a residual foot extending to 75 and 80 K in both samples (Fig. 1). This admixture of the $N=2$ and $N=3$ phase, which is in accord with previous studies,^{3,5,7,8} complicates the analysis of the Hall data. The Tl samples show an onset temperature near 130 K (in ρ vs T). Zero resistance is observed at 116 K (in sample T1) and at 123 K (in T2).

The Hall voltage V_H was measured as in a previous study¹² on $La_{2-x}Sr_xCuO_4$ by rotating the samples in a magnetic field fixed at 8 T, and fitting the observed varia-

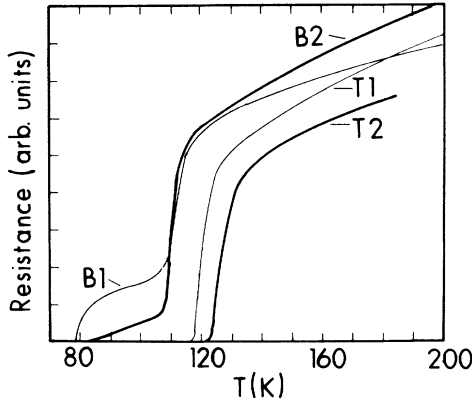


FIG. 1. Resistance of the four samples used in the Hall effect study. Samples B1 and B2 contain mixtures of both the 2:1:2:2 and 2:2:2:3 phases of Bi-Ca-Sr-Cu-O while samples T1 and T2 are single-phase $Tl_2Ca_2Ba_2Cu_3O_x$.

tion of V_H vs ϕ (angle of rotation) to a sine curve. The current I was typically 80 mA. At some temperatures I was halved to check that V_H is linear in I . We estimate our temperature stability to be ± 0.05 K during the course of a rotation. At each T we find that the scatter in the plot of V_H vs ϕ is under 5% so that V_H is determined to this level of uncertainty. However, in the T1 samples we found a slight history dependence which produces a shift in V_H as large as 10% after a 20 K cycling in T . This irreproducibility is responsible for most of the data "scatter" for the two T1 samples. We believe these changes to be caused by thermally induced relaxations of grain positions which alter the current paths. The T1 sinters were not subject to as high a pressure during the pelletization as used for other ceramics. No history-dependent shifts were detected in either Bi sample. In all samples R_H is positive (holelike).

For the Bi samples the most interesting features of the Hall data are the temperature dependence and the overall magnitude (Fig. 2). The solid line is a fit of R_H to a $1/T$ behavior, which is reminiscent of that observed in ceramic

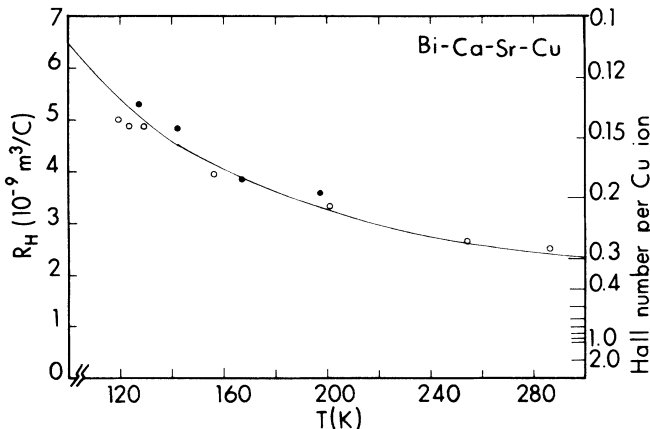


FIG. 2. The Hall coefficient R_H vs temperature T of samples B1 (open) and B2 (solid circles). The solid line is the curve $R_H = 640/T$ ($10^{-9} \text{ m}^3/\text{C}$).

1:2:3 and in single crystals of 1:2:3 (with field normal to the a - b plane.) The single-crystal result on 2:1:2:2 Bi reported by Takagi *et al.*¹⁶ shows a less pronounced T dependence as well as a value of R_H approximately half as large as our results. The $1/T$ dependence, which is problematical in a single-band model, has not received a satisfactory explanation in $YBa_2Cu_3O_7$. (Two-band Drude-Boltzmann models with rather specific compensation conditions have been proposed to account for the R_H vs T behavior.¹⁷) However, it is unlikely that the same band-structure occurs in the Bi compound and 1:2:3. Band-structure calculations show the presence of simply connected pockets at the Fermi surface (FS) associated with the Bi planes, but no $1d$ bands. Therefore, the existence of a $1/T$ variation in R_H in both the 1:2:3 and Bi-compounds implies a more universal mechanism which is currently not understood. It is unlikely to be an artifact of multiple bands crossing the FS since it occurs in systems with such disparate FS. Recent work¹⁸ on the 2:1:4 system (with $x=0.15$) shows that R_H also decreases with increasing T , although less strongly than $1/T$. In both 1:2:3 and 2:1:4 systems the introduction of dopants which suppress T_c also suppresses the $1/T$ variation of R_H .¹⁸ The growing evidence indicates that the linear behavior of n_H vs T is a characteristic signature of the current carrying excitations within the CuO_2 planes, which cannot be explained within the framework of normal Fermi-liquid theory. The unusual Hall scattering may arise from the formation of singlet holes in the d^9L configuration. A large body of evidence points to strong Coulomb interaction between the carriers and the importance of correlation effects in understanding the normal-state properties. Theoretical work¹⁹ based on the Hubbard model also anticipates such differences in the normal-state properties. The Hall effect, together with the ubiquitous linear ρ vs T behavior, may be the most striking anomalies in the normal state.

A comparison of the overall magnitude of R_H in Fig. 2 with that found in $YBa_2Cu_3O_7$ ceramics shows that R_H is almost a factor of 3 larger in the Bi compounds. (Most reported Hall data^{14,15} on 1:2:3 ceramic show R_H decreasing from $2 \times 10^{-9} \text{ m}^3/\text{C}$ at 100 K to $6 \times 10^{-10} \text{ m}^3/\text{C}$ at 300 K.) On the right-hand scale in Fig. 2 we have shown the filling factor ν defined as n_H ($=1/R_H e$) normalized to the number of Cu ions present in the compound. (We have used the lattice parameters appropriate for the 2:1:2:2 member. This is slightly inaccurate since there is an admixture of the 2:2:2:3 member present in both samples.) At 100 K ν extrapolates to 0.12. For comparison, in 1:2:3 Wang *et al.*¹⁴ infer a value for ν equal to 0.25 at 100 K while the equivalent number from Tozer *et al.*²⁰ equals 0.5 (corresponding to one hole per unit cell in 1:2:3.) Thus, ν (inferred from the Hall number) is a factor of 2 to 4 smaller in the Bi system.

A small filling factor of similar magnitude is also obtained for the T1 samples (Fig. 3). Here we have used lattice parameters appropriate for the 2:2:2:3 member since T_c is 120 K. Between 125 K and 280 K ν increases from 0.1 to 0.15. The slight T dependence of R_H is apparently weaker than in Fig. 2. However, a $1/T$ dependence cannot be totally excluded at this stage because of the scatter

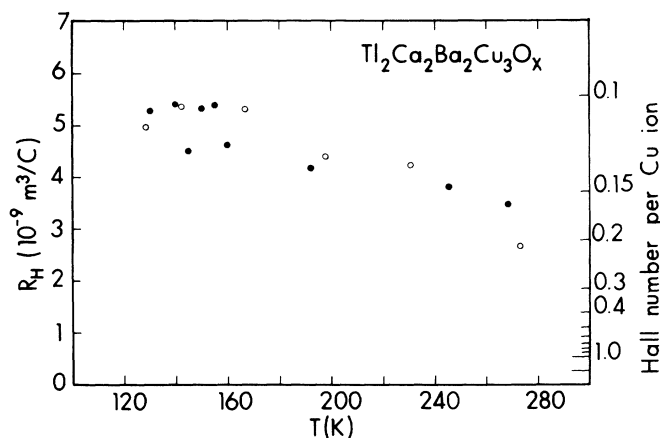


FIG. 3. The Hall coefficient R_H vs T for samples T1 (open) and T2 (solid circles). The scatter in the data which exceeds our measurement uncertainty is caused by shifts in the signal caused by thermal cycling.

caused by temperature cycling.

Because a definitive study of the Hall effect requires good single crystals, the ceramic data reported here can only provide a qualitative picture of the carrier density. (It is likely that corrections for the effects of conductivity anisotropy and sample porosity will lead to a rescaling of the absolute magnitudes of R_H .) Nonetheless, it is interesting to compare the data here with the corresponding ceramic data on the 2:1:4 and 1:2:3 systems. The filling factor ν provides a convenient yardstick when we compare the four families. In the 2:1:4 system ν (experimentally equal to x in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ for $x < 0.15$) can be inter-

preted as the number of itinerant holes per Cu ion. For low x , T_c is observed to scale linearly with ν , reaching a maximum of ~ 36 K at $x = 0.15$. In $\text{YBa}_2\text{Cu}_3\text{O}_y$ ν [defined normalized to the Cu(2) ions] is found to be larger (0.25 or 0.5 at 100 K), consistent with the higher T_c observed in the 1:2:3 system. (A strict adherence to the linear relationship would require $\nu = 0.36$.) However, in the two new families ν is much smaller than expected from a direct application of the T_c vs ν relationship. This is especially evident in the Tl compound where ν at 100 K is 3–4 times smaller than in $\text{YBa}_2\text{Cu}_3\text{O}_7$, whereas T_c is 30% higher. If we identify n_H with the actual carrier concentration n , the Hall results would imply that the T_c enhancement occurs *despite* an apparent decrease in the overall filling factor (compared with 1:2:3). This would suggest that the enhancement in T_c is predominantly due to the increase in the number of consecutive CuO_2 planes, as suggested by previous studies which found a correlation between T_c and N in the two new families.⁹ However, the interpretation $n_H = n$ is rather uncertain at present, especially in the high- T_c oxides which show strong variation of R_H with T . As discussed above there is growing evidence that the $1/T$ variation in R_H in the superconducting oxides has an unconventional origin, so that the actual relation between R_H and n remains to be worked out.

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