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Hall-effect anomaly in the high-T_c copper-based perovskites

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The temperature (T) dependence of the Hall coefficient R_H is studied in Co-doped and Ni-doped $YBa_2Cu_3O_7$, and Ni-doped $La_{2-x}Sr_xCuO_4$. In these systems we show that as the high-T_c behavior is suppressed, the unusual T dependence of R_H is also suppressed in a characteristic way. The evidence strongly suggest that the strong T dependence of R_H is an anomaly specific to the unconventional normal state in most, perhaps all, of the high-T_c oxides.

An important question regarding the high-T_c superconducting oxides[1] $La_{2-x}Sr_xCuO_4$ (2:1:4), $YBa_2Cu_3O_7$ (1:2:3), Bi-Sr-Ca-Cu-O (Bi 2:2:1:2 or 2:2:2:3), and Tl-Ba-Ca-Cu-O is whether conventional normal Fermi-liquid theory can account for the electronic properties in the normal state.[2] Anderson and co-workers[2,3] and Fukuyama and Hasegawa[4] have emphasized that anomalous deviations from familiar Fermi-liquid behavior are to be expected because the charge carriers are strongly correlated, and one has to start from a ground state different from a Fermi liquid. In contrast, several attempts[5,6] have been made to explain the transport data using conventional Bloch-Boltzmann models based on band structure. The linear temperature (T) dependence of the resistivity ρ has been widely discussed in this context.[3] Here we present experimental evidence that the Hall effect is also strikingly anomalous in the high-T_c oxides containing CuO_2 sheets. By studying the Hall coefficient R_H in a large range of samples under different doping conditions we infer that there is a distinct correlation between the characteristic[7-9] R_H vs T profile and high-T_c behavior. (In 1:2:3 the T dependence is strong: $R_H \sim 1/T$; in other high-T_c oxides the T dependence is weaker.) When the superconductivity is suppressed by dopants we find that the slope of n_H vs T ($n_H = 1/eR_H$) is suppressed as well. The correlation follows a similar pattern in both Ni- and Co-doped $YBa_2Cu_3O_7$ as well as in $La_{2-x}Sr_xCuO_4$ doped with Ni. The accumulated evidence suggest that a T dependent n_H is a generic property of an unusual ground state that occurs in most (possibly all) of the high-T_c oxides comprised of CuO_2 planes, and *not* an accident of particular band arrangements, or overlapping bands. Furthermore, the T dependence of n_H is suppressed whenever T_c is reduced by chemical doping.

The Ni- and Co-doped 1:2:3 samples are from the same pellets as the samples previously studied using structural, chemical, and magnetic measurements.[10,11] Powder x-ray diffraction verified all samples to be single phase. For two doping levels of the Co-doped $YBa_2Cu_3O_7$ samples ($x = 0.2$, 0.8), the Co sites and the oxygen content were determined by neutron powder diffraction.[11] From the neutron results Co is known to substitute for Cu(1) (chain sites). Thermogravimetry data indicate that Ni substitutes for Cu(2) (plane sites).[10] The carrier density n is dramatically decreased with Co doping whereas it is not significantly affected by Ni doping.[12]

Figure 1 shows the T dependence of n_H (per unit cell) for the Co-doped samples ($x = 0.02$, 0.05, 0.1, 0.2, and 0.3.) As in undoped $YBa_2Cu_3O_7$, n_H in the $x = 0.02$ sample shows a distinctive linear-T dependence which extends to 300 K. The trend in Fig. 1 suggests that as x increases, the average slope dn_H/dT decreases until it becomes negligible at large x. Over the same range of x, T_c decreases sharply from 93 to 22 K (for $x = 0.3$).[10] If the observed

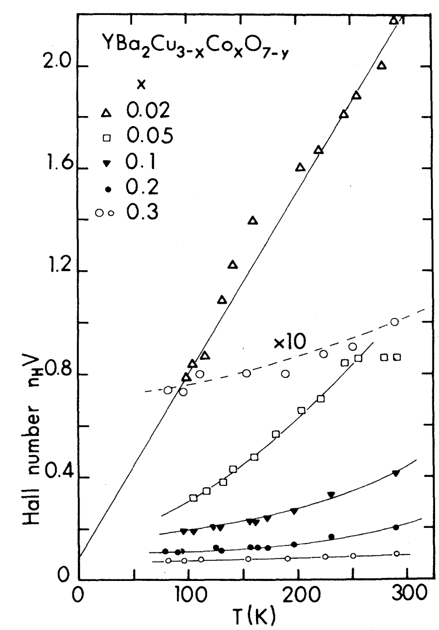

FIG. 1. Variation of the Hall number (defined as V/R_He where V=unit-cell volume, 175 Å^3) with temperature in Co-doped $YBa_2Cu_3O_7$. The data for $x = 0.3$ (open circles) is replotted enlarged by a factor of 10 to show the weak T dependence. The slopes rapidly decrease as x increases. Lines are drawn to guide the eye. See Refs. 10 and 11 for T_c vs x.

n_H is T independent it is a reasonable assumption that n_H provides a reliable estimate of n. Thus, for the $x=0.3$ sample we infer that n is close to 0.07 holes/cell, which implies that Co doping dramatically reduces the itinerant hole population. (Further discussion of this point appears in Ref. 12.)

In the limit $x \rightarrow 0$, however, the strong T dependence of R_H makes any attempt to extract n from n_H problematical. We argue below that the strong T dependence arises from an anomalous Hall current associated with the carriers responsible for the high-T_c instability. The anomalous Hall scattering obscures the ordinary Hall current, which can only be detected when the high-T_c mechanism is suppressed.

In Ni-doped 1:2:3, T_c also decreases with increasing x, although to a lesser degree at large x ($T_c \sim 58$ K at 0.4.) In Fig. 2 we show the variation of n_H vs T for the Ni-doped samples. As in Fig. 1 we find that the linear T behavior of n_H (dashed line in Fig. 2) is rapidly converted to a less T-dependent curve as x increases from 0.02 to 0.4. To highlight the suppression of the T dependence, we plot in Fig. 3 (top curve) the variation of the slope dn_H/dT at 100 K with x. As x increases to 0.4, the slope decreases by a factor of 4. However, in contrast with the Co case, the overall change in the value of n_H at 100 K is rather slight. For the $x=0.4$ sample, the curve appears to saturate at low T to a value slightly less than 1 hole/cell (compared with 0.07/cell for the $x=0.3$ sample in Fig. 1). This point is emphasized by plotting n_H vs x at several fixed T (see Fig. 3). Although the curves show an interesting peak near $x=0.05$, they all converge to the value $n_H \sim 1$ hole/cell at high x. Also shown in Fig. 3 (dashed line) is the extrapolated value of n_H as $T \rightarrow 0$. We next argue that the data in Fig. 3 enables us to deduce n in "pure" $YBa_2Cu_3O_7$. When x exceeds ~ 0.3, the anomalous T dependence of n_H is removed, so that we can identify n_H with n. Further, since Ni doping does not change the hole density, we infer that n in undoped 1:2:3 equals the value n_H observed in the $x=0.4$ sample, i.e., 1 hole/cell. (In effect, Ni doping enables us to suppress the anomalous T dependence without changing n.) Thus, the two cases (Co and Ni) suggest similar trends: When the conditions favorable to high-T_c superconductivity are removed the anomalous linear n_H vs T behavior is also suppressed, leaving only a T-independent Hall resistivity. Similar considerations[13] apply to the Hall effect in oxygen-doped[9] $YBa_2Cu_3O_{7-y}$.

Previous studies of the Hall effect[14-16] in the 40-K system $La_{2-x}Sr_xCuO_4$ found that R_H is T independent at low concentrations of Sr ($x<0.1$). On the basis of the data in Figs. 1 and 2, we were encouraged to search for a similar pattern of behavior in the 40-K system. Published work[17] shows that, at a fixed Sr concentration $x=0.16$, very slight amounts (y) of Ni suppress T_c from 38 K ($y=0$) to under 4 K (at $y=0.05$). Our data on n_H for four samples within this doping range are shown in Fig. 4. In the absence of Ni ($y=0$), n_H increases by 67% as T increases from 50 to 200 K. However, when Ni is added, the slope dn_H/dT is systematically suppressed, in accord with our expectations. As in Fig. 2, n_H is independent of y at low T; this again suggests that Ni does not change n

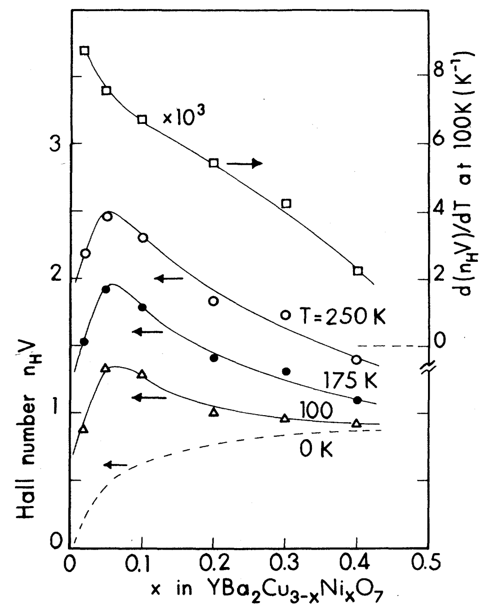

FIG. 3. Top curve: Variation of the slope $d(n_HV)/dT$ at 100 K with x in $YBa_2Cu_{3-x}Ni_xO_7$. Lower curves: Variation of the Hall number with x at constant temperature. The data points are interpolations of measurements reported in Fig. 2. The dashed line indicates the extrapolation of the data to $T=0$. In the text, the strong suppression of the slope with x is interpreted as quenching of the anomalous contribution to the Hall current. At high x, only the normal Hall current component remains.

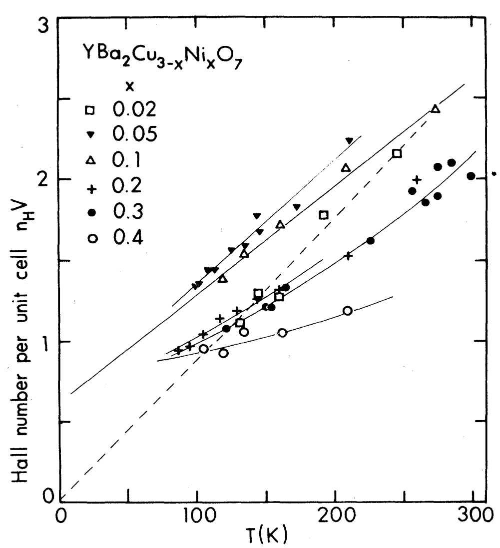

FIG. 2. Variation of the Hall number with temperature in $YBa_2Cu_{3-x}Ni_xO_7$. The dashed line is drawn through the data for the $x=0.02$ sample. Solid lines are drawn through the data for higher concentration samples. The slopes rapidly suppressed as x increases. However, the Hall number at $x=0.4$ remains fairly large (~ 1 hole/cell) unlike the Co case. See Ref. 12 for T_c vs x.

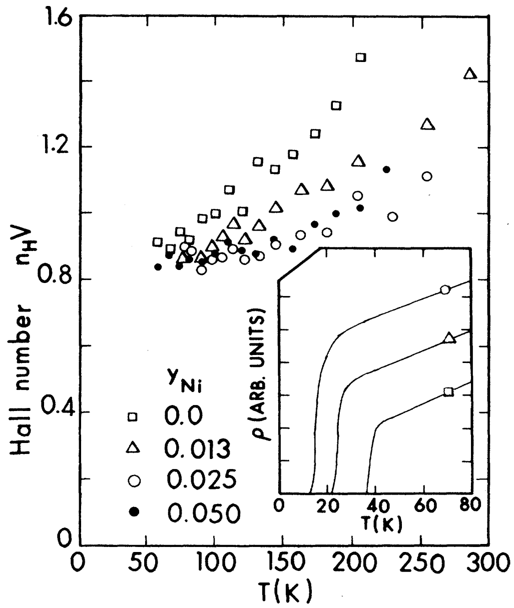

FIG. 4. The temperature dependence of $n_H V$ (V=190 Å^3) in four samples of $La_{2-x}Sr_xCu_{1-y}Ni_yO_4$ (x=0.16). As in Fig. 2, the slope dn_H/dT is systematically suppressed as T_c decreases. The ρ vs T profile (inset) shows that the slope $d\rho/dT$ is unchanged by Ni doping (content indicated by symbols). The T_c's are 37, 24, and 15 K.

despite the strong effects on T_c and dn_H/dT. [The small amount of Ni (< 5%) needed to suppress the slope in Fig. 4 also argues against a band-filling mechanism. Instead, we propose that the Ni impurities are disrupting a coherent scattering effect which is responsible for both the anomalous Hall current and the high-T_c instability.]

In all the known high-T_c oxides based on CuO_2 planes, R_H is positive and decreases with increasing T. In "two-plane" Bi-2:2:1:2 with T_c=85 K, Takagi *et al.*[18] have shown that the decrease in R_H is weaker than $1/T$. For the "three-plane" systems based on Bi and Tl, R_H also decreases with increasing T, but sample difficulties preclude an accurate determination of the T dependence.[19] At present the importance of several factors affecting T_c (such as the interlayer coupling strength, doping conditions, in-plane lattice disorder, and n itself) remain to be sorted out. Hence, we are unable to compare meaningfully the magnitude of the slope dn_H/dT in different compounds, even those with similar T_c's. Nonetheless, for each compound separately, dn_H/dT is strongly correlated with T_c. (See note added below on Bi-2:2:1:2.)

By itself, the prevalence of a T dependence in n_H in the high-T_c oxides can only suggest that this transport property should be regarded as a property intrinsic to high-T_c systems. What we have shown here is that the converse is true as well. When high-T_c behavior is intentionally suppressed in a particular compound, the T dependence of n_H is also removed. These two conditions, applying to systems with rather different band structures, pose severe difficulties for Bloch-Boltzmann theories which attempt to explain the T dependence of n_H using fortuitous cancellation in multiple bands.[6] (It is unlikely that such accidental cancellations occur both in 1:2:3, as well as in 2:1:4 which has CuO_2 planes only. Further, we point out that the compensation models,[6] with roughly equal σ_{xy} for electrons and holes, predict that as the chemical potential is raised by doping, the electron pocket should expand at the expense of the hole pocket. Thus, R_H should decrease towards negative values, in contradiction with the data in Fig. 1. This argument persuades us that in 1:2:3, only one band contributes to the electronic transport.) In the limit of strong suppression of T_c what is the nature of the ground state? Since the ρ vs T profile remains linear in T (down to 20 K in Fig. 4, inset), the evidence suggests that the system remains "unconventional." The low-temperature transport properties of this unconventional system is largely unknown.

In the opposite direction of decreasing impurities, the T dependence of n_H becomes more pronounced as T_c increases in all the cases studied. We speculate that the strong T dependence arises from an anomalous Hall current which dominates the conventional Lorentz term. The anomalous term may arise from an as-yet unknown asymmetric scattering mechanism associated with the unusual spin-zero current-carrying excitations discussed below, and is thus specific to the particular ground state of these unusual oxides. The anomalous Hall component is unlikely to receive an explanation using conventional Fermi-liquid theory, which ignores the effects of strong correlation. [Because R_H neither varies as χ (susceptibility) nor as ρ^2, we also do not think that conventional magnetic skew scattering can account for the anomalous behavior.]

We next discuss a scenario for the Ni doping which is suggested by the Hall data. In undoped $YBa_2Cu_3O_7$ there is one itinerant hole per cell, which goes into the planes,[12] (i.e., Cu ions on chain sites are all in the +2 state, consistent with neutron scattering results[11]). The hole, which resides in states mainly $2p$ in character,[20] forms a d^9L orbital around a Cu(2) ion. If the Ni impurity is divalent (d^8) the number of ligand holes must remain unchanged because the chemical potential is pinned by the reservoir of electrons in the $2p$ ligand states. [Cu(2) ions at other sites pick up a formal valence of +3.]

Zhang and Rice, and Eskes and Sawatsky[21] have shown that with hybridization the ligand hole forms a *singlet* state with the $s=\frac{1}{2}$ spin on the Cu site which is more deeply bound than the nonbonding state. The effective Hamiltonian reduces to the single-band Hubbard model, in agreement with Anderson's original picture.[2] We next consider the hybridization at a Ni^{2+} impurity site. Because the $3d$ level of Ni is situated much higher than Cu($3d$), the $3d$-$2p$ hybridization is greatly reduced, and the singlet bound state with a ligand hole is not energetically favorable, i.e., the Ni site becomes *inaccessible* to the singlet hybrid state. If we assume that this singlet state is essential to both the high-T_c superconductivity *and* the anomalous Hall current, we can correlate the Hall data with the destruction of the singlet band by the proliferation of inaccessible sites. [The superconductivity may be quite sensitive to the loss of available sites because of the unusually short coherence length ($\xi \sim 10$ Å).]

Note added. After completion of this work we learned of the data of Matsuda *et al.*[22] on n_H in Pr-doped 1:2:3, which also show the slope suppression of n_H vs T with increasing dopant content, as discussed here. We have also extended[12] the doping study to $Bi_4Sr_3Ca_{3-x}Tm_xCu_4O_{16+y}$, and find that as x(Tm) increases, n_H decreases linearly, extrapolating to zero at $x = 1.4$. The correlation between the slope dn_H/dT and T_c discussed here is also verified in this system.

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