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Hall effect of $La_{2-x}Sr_xCuO_4$: Implications for the electronic structure in the normal state

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The Hall effect has been measured at 77 K in $La_{2-x}Sr_xCuO_4$ for the range of x in which high-temperature superconductivity is observed. Below $x=0.15$, $1/R_H$ increases linearly with x consistent with one itinerant hole per Sr atom. (The carrier density is 2.1×10^{21} cm^{-3} at $x=0.15$ where the superconducting transition temperature is a maximum.) Between 0.15 and 0.18, R_H drops by a factor of 30, remaining undetectable for larger x. Proposed charge-density-wave models are in conflict with the data.

There has been considerable interest in the electronic structure of the oxides $La_{2-x}M_xCuO_4$ (M=Sr, Ba) since the report by Bednorz and Müller[1] of the observation of superconducting behavior in $La_{2-x}Ba_xCuO_4$ at temperatures above 30 K. Uchida, Takagi, Kitazawa, and Tanaka[2] obtained the single phase of $La_{2-x}Ba_xCuO_4$ corresponding to the K_2NiF_4 structure. Several workers[3-6] have subsequently confirmed the bulk nature of the superconducting state in both the $La_{2-x}Ba_xCuO_4$ and $La_{2-x}Sr_xCuO_4$ systems. The underlying mechanism for the unusually high superconducting transition temperature T_c is at present the subject of intensive research.

The pure compound La_2CuO_4 undergoes a structural transition[7] at $T_d=533$ K from the tetragonal to orthorhombic (T'-O) phase. As the concentration of Sr increases the T'-O transition temperature (T_d) is rapidly suppressed[8] and the resistivity versus T profile changes from activated to metallic behavior. T_c increases as x varies from 0.10 to 0.15 reaching a maximum[4] of $\sim$40 K for x near 0.16. For x greater than 0.16 the relative volume of superconducting phase declines precipitously.[4,8] Recently, several models have been proposed for the normal state, such as the charge-density-wave state (CDW),[9] and the resonating valence-bond (RVB) state.[10] To help clarify the problem we have measured the Hall effect in eight samples of $La_{2-x}Sr_xCuO_4$ which span the composition range $0.05<x<0.25$. The Hall constant R_H is found to be positive (hole conduction). For x below 0.15 we find that R_H varies as $1/x$, i.e., the carrier density increases linearly with x. However, within a fairly narrow range $0.15<x<0.18$, R_H decreases by a factor of 30 and remains unobservable for $x>0.2$.

Samples were grown as described in Ref. 4 for La_2O_3, CuO, and $SrCO_3$, each 99.999% pure. The powders were pressed at 7 kbar into pellets $\frac{1}{2}$ in. in diameter and reacted in a Pt boat in a furnace under flowing oxygen at 1120°C for 36 h. The pellets were cut and polished into rectangular bars of size $2.5\times6\times0.23$ mm. Most of the measurements were performed with the sample inside a superconducting magnet with a maximum field B of 15 T. The variation of the dc Hall voltage V_H was obtained by rotating the sample through an angle θ about an axis parallel to the current. (Figure 1: At $\theta=0$, B is normal to the plane of the sample.) Joule heating and thermomagnetic effects were minimized by immersing the sample in liquid nitrogen. To verify the linearity of the Hall signal we also performed measurements of V_H vs B in a Bitter magnet. To obtain adequate signal to noise discrimination, B was held fixed at selected values and the output of the nanovoltmeter (Keithley 181) averaged. For samples in which the two techniques could be applied good agreement was obtained for R_H. For samples with $x>0.17$ the Hall signal is very weak. We swept the Bitter magnet to its maximum field in 1 min and measured V_H at the three

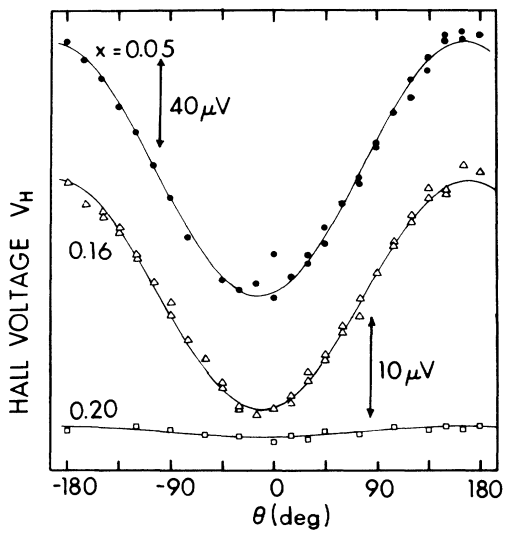

FIG. 1. Variation of the Hall voltage with angle θ (between the field B and the normal to the plane of the sample). The rotation is about an axis parallel to the current. Data at 15 T from three samples ($x=0.05$, 0.16, and 0.20) are shown. The current is 208 mA for the $x=0.20$ sample and 100 mA for the other two. The vertical scale indicated is 40 μV (10 μV) for the solid (open) symbols.

values 15, 0, and −15 T. The average of five such runs was used to estimate V_H. If the standard deviation for either field orientation exceeded the average we regarded the Hall signal to be undetectable. We estimate that the smallest detectable value for R_H is $\pm 2\times10^{-10}$ m^2/C.

The variation of R_H ($=V_H t/IB$) vs x is shown in Fig. 2 for the six samples in which a detectable signal was obtained. The two samples ($x=0.20$ and 0.25) for which R_H was undetected are also indicated by vertical bars. The solid line represents the variation of R_H calculated assuming that each Sr dopant denotes one itinerant hole. The measured Hall signal is consistent with a hole density of 4.9×10^{20} cm^{-3} and 2.1×10^{21} cm^3 for $x=0.05$ and $x=0.15$, respectively. (The mobilities are 1.6 and 4.3 cm^2/Vs, respectively.) In the small range between 0.15 and 0.18, R_H rapidly decreases in magnitude by a factor of 30, deviating strikingly from the solid line. For compositions x larger than 0.2 the Hall signal is below our level of detection, indicating the existence of a different electronic structure (or phase) of the system rather than a simple zero crossing of R_H. The bulk resistivity ρ measured on the same samples at 77 K (Fig. 2, open symbols) shows a fairly smooth variation as x exceeds 0.175. The abrupt decrease in R_H occurs very near the T′-O line which separates the tetragonal from the orthorhombic phase (Fig. 2, inset). Both the onset temperature for superconductivity and the midpoint transition temperature T_c for these samples are given in Ref. 4 (T_c equals 26.0, 40.3, 35.9, and 31.2 K at $x=0.1$, 0.15, 0.20, and 0.25, respectively). A more useful indicator of the superconducting phase is the fractional volume showing the Meissner effect versus x. This has been reported by Fleming, Batlogg, Cava, and Rietman.[8]

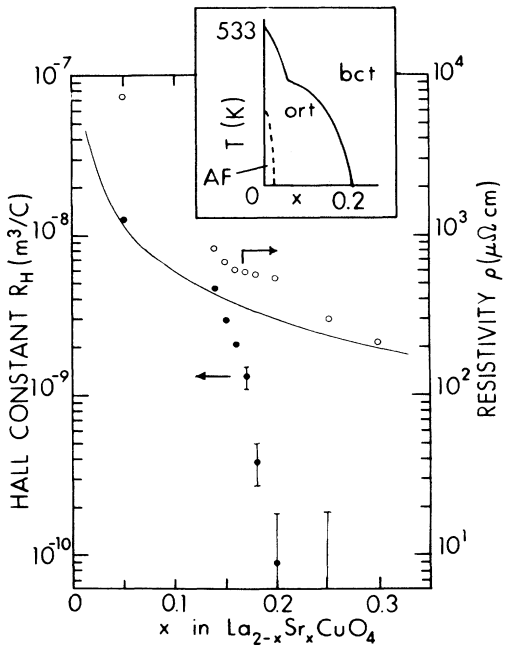

FIG. 2. (Main panel) The Hall constant vs x in $La_{2-x}Sr_xCuO_4$ at 77 K (solid circles). The solid line is the equation $1/R_He=2x/(abc)$ (one carrier per Sr atom). The open circles show the ρ at 77 K measured in the same samples. (Inset) Phase diagram showing the tetragonal (bct), orthorhombic (ort), and antiferromagnetic (AF) phases (adapted from Refs. 6 and 11). The solid line is the variation of T_d vs x.

First we shall compare our data with predictions of rigid-band models, assuming zero electron-electron Coulomb interaction ($U=0$). In the spirit of such models the conduction band is half-filled (one hole per Cu ion, corresponding to a density of 1.1×10^{22} cm^{-3}) in the tetragonal phase ($T>T_d, x=0$). The Fermi level lies midway in the band formed from the antibonding (Cu) $d_{x^2-y^2}$ and (O) p states. The Fermi surface (FS) lies fairly close to a square with sides parallel to the 110 direction if dispersion in the c direction is neglected. At T_d a structural transition occurs which induces a buckling of the Cu octahedra along the 110 direction. At first sight one expects this distortion to open up a gap in the 110 direction, and the Fermi surface which coincides with the boundaries of the new Brillouin zone (BZ) to be destroyed. However, the buckling appears to have the wrong symmetry to induce a gap at the FS, although such a gap undoubtedly exists in the pure compound which is semiconducting below 100 K. Thus the origin of the gap is strongly debated. [A further complication is the appearance of an antiferromagnetic (AF) phase below 240 K in the pure compound.[11]] On the basis of the Hall data we shall argue that this gap *persists* throughout the doping range $0.05<x<0.17$, remaining pinned to the 110 planes. The implication is that it is *unlikely* to be due to Fermi-surface-driven instabilities such as a conventional charge (or spin) density wave.

As x is increased from 0, hole pockets are created at the corners of the first BS (Fig. 3, upper panel). Because the energy dispersion is nearly two dimensional, the area of these pockets increases linearly with the itinerant hole population. Thus, $1/R_He$ is positive and equal to the Sr concentration $2x/(abc)$ for $x<0.15$ (where $e>0$ is the electronic charge and a, b, and c are the lattice parameters). The one itinerant hole per Sr atom rule implies that the gap which existed over the whole FS in the pure compound remains unaffected despite heavy doping ($x<0.15$), which drops the Fermi level considerably. In particular, the Hall data are incompatible with the destruction of a CDW state within this compositional range. (In proposed CDW models[6,9] the CDW exists in the pure compound. Light doping destroys the CDW.) The destruction of the CDW would restore large portions of the FS in the normal state and increase the free carrier density to large values (10^{22} cm^{-3}). This is clearly not seen in the data. (The scenario in which the spanning vector of the CDW changes with x to optimize nesting is also unlikely since the Hall constant arising from the ungapped portions of the FS would not scale as $1/x$, in general.) There remains the possibility that the CDW wave vector remains pinned at the commensurability value (110) until x increases to 0.17. This would be consistent with our data. However, one would need to justify how the conventional Peierls state is stabilized despite sacrificing most (> 50%) of the free energy gained from electrons at the FS. The CDW model is unlikely in this system unless a way is found to circumvent these difficulties.

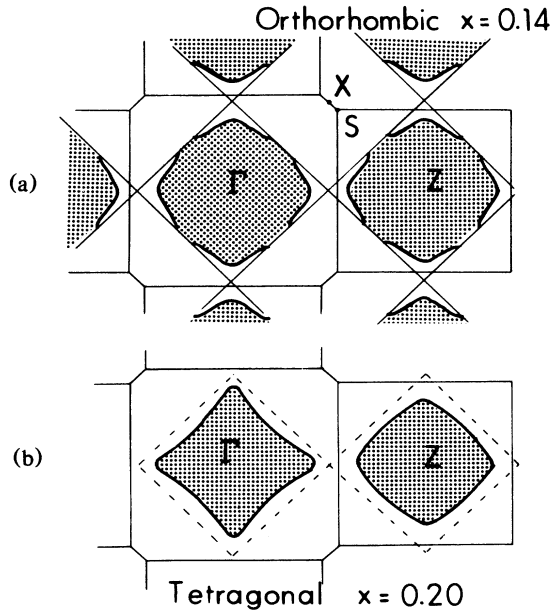

FIG. 3. (a) (Upper panel) The extended zone scheme of the orthorhombic phase showing the Fermi surface at a concentration of $x=0.14$ (assuming $U=0$). A hole pocket in the first BZ with a population of 1×10^{21} cm^3 is schematically indicated. Gaps parallel to the 110 directions are assumed. (b) (Lower panel) Extended zone scheme at a filling of $x=0.20$. A plausible explanation for the abrupt decrease in R_H (within $U=0$ models) is the change in FS topology from small hole pockets to a large electron FS centered at Γ (see text). The electron FS corresponds to a density of 8.5×10^{21} cm^{-3}.

The striking feature in Fig. 2 is the rapid decrease of R_H to a value below our resolution as x increases beyond 0.15. Because the decrease occurs ($x=0.17$) near where the T′-O transition line intersects our working temperature (Fig. 2, inset), it appears plausible that the T′-O transition drastically affects the topology of the FS so that the relatively small hole pockets are transformed into large electron pockets. This is schematically represented in Fig. 3 (lower panel). The large electron pockets with a total volume close to 10^{22} cm^{-3} would imply that R_H is negative and $\sim -6\times10^{-10}$ m^3/C. This would reproduce the sharp decrease in R_H although not quite the magnitude that is observed. A serious difficulty with this model is that for samples with $x=0.15$, T_d occurs at 190 K. Measurements of R_H vs T show no observable change as T crosses T_d, suggesting that the transition at T_d does not affect the FS. (This difficulty together with the expectation discussed above that the distortion at T_d lacks the symmetry to induce gaps in the 110 direction persuades us that the T′-O structural distortion neither causes the gap in the pure compound nor the sharp drop in R_H near $x=0.17$.)

We should point out that even if the gap in the 110 direction is unaffected by the T′-O distortion it is still possible to account for the sharp drop in R_H within the ($U=0$) rigid-band model. At the doping level $x=0.17$ the hole pockets centered become large enough to coalesce, converting the FS into one large electron pocket centered at Γ [Fig. 3(b)]. The change in topology again leads to a sharp decrease in R_H. Note that this change in FS topology is not expected if we change T at fixed x, in agreement with experiment.

In view of the very strong evidence for a large U in the pure compound we next discuss our data in this limit. A Mott-Hubbard gap exists at the chemical potential in the $\frac{1}{2}$-filled system if U is large (one localized hole on each Cu ion in the pure compound). The electrons are localized because of the strong intrasite repulsion. Increasing the Sr concentration drops the chemical potential below the $\frac{1}{2}$-filled level, creating holes which are itinerant. Thus, the $x=0$ compound is semiconducting at low T with an activation energy of $U-4t$ (where t is the hopping integral). With increasing x the system becomes metallic with a carrier concentration equal to the Sr concentration. The T′-O distortion is irrelevant to the Mott-Hubbard gap (so that R_H is not affected by increasing T above T_d in, say, the $x=0.15$ compound). This scenario is quite consistent with the transport data for $x<0.15$, and provides a natural framework for the one itinerant hole per Sr atom rule described above. Furthermore, the thermopower S in the doped system[12] ($S\sim30$ μV/K at 77 K for $x=0.15$) is consistent with a strongly correlated system, rather than a wide band metal.[13] (The recent observation[11] of an AF state in the $x=0$ compound at 240 K is also consistent with a large U.) The challenge in this model is to explain the sharp drop in R_H at $x=0.17$, which remains perplexing. The RVB model[10] of Anderson and co-workers proposes that the introduction of a low density of holes into the $\frac{1}{2}$-filled AF state destroys the AF state, replacing it with a state of resonating valence-bond pairs. In this picture the itinerant holes are responsible for the current transport and the Hall signal. Our data raise the interesting possibility that the sharp drop in R_H at $x=0.17$ signals a doping-induced transformation of the RVB state.

In summary, the Hall data are inconsistent with the destruction of a CDW or spin-density wave state in the range $x<0.17$. An incommensurate CDW state with a wave vector which shifts with x is also ruled out. We have also argued that the T′-O distortion is probably irrelevant to changes in the electronic properties. In contrast, the variation of R_H vs x (for $x<0.15$) is consistent with a large-U model with a Mott-Hubbard gap in the $\frac{1}{2}$-filled system. However, the rapid decrease in R_H at $x=0.17$ remains to be accounted for.

Note added. After this work was completed we learned of the Hall effect data on $La_{2-x}Sr_xCuO_4$ by Uchida *et al.*[14]

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