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Approaching the Mott-Hubbard insulator in the 85-K superconductor $Bi_2(Sr,Ca)_3Cu_2O_{8+d}$ by doping with Tm

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As x increases in $Bi_4Sr_3Ca_{3-x}Tm_xCu_4O_{16+y}$ the Hall carrier density n_H decreases linearly. The variation is consistent with Mott-Hubbard behavior, but in conflict with band-structure results which ignore correlations. We find that the variation of T_c vs n_H is nonmonotonic. The source of the large carrier population (0.4/Cu) in the undoped ($x=0$) compound is discussed.

The recently discovered superconductors based on Bi-Sr-Ca-Cu-O strongly resemble $YBa_2Cu_3O_7$ (called 1:2:3) and $La_{2-x}Sr_xCuO_4$ (2:1:4) in structure.[1-4] In particular, the $N=2$ member $Bi_2(Sr,Ca)_3Cu_2O_{8+d}$ (2:2:1:2), which has a transition temperature T_c near 85 K, is similar to the 1:2:3 structure, with the Bi-O bilayer replacing the Cu(1) chains (N is the number of adjacent CuO_2 planes). The structural similarity raises a number of interesting questions on the variation of T_c and the carrier density n as the chemical potential μ is raised by chemical doping. If strong correlation (large U) exists in the Bi compound the behavior of n vs μ should imitate the behavior found in the 2:1:4 and 1:2:3 systems.[5-8] On the other hand, if U is negligible, band-structure calculations should give a satisfactory account of the variation of n vs μ. A second question concerns the role of the Bi-O planes. Band-structure calculations,[9,10] which ignore correlations, indicate that a band associated with Bi-O intersects the Fermi level. This raises the important issue of whether the superconducting carriers also exist in the Bi-O planes.

To address these questions we have performed Hall and resistivity measurements on a series of well-characterized polycrystalline samples of $Bi_4Sr_3Ca_{3-x}Tm_xCu_4O_{16+y}$ (4:3:3:4). Thulium was chosen because it readily formed single-phased compounds (see Ref. 11). Samples from the same pellets were previously studied using x-ray thermogravimetric analysis (TGA) and magnetization measurements.[11] Crystallographic size and the Curie-Weiss susceptibility results show that the Tm dopants are trivalent. The oxygen content versus x has also been measured by TGA. Several studies on the effect of cationic substitution have been reported previously.[12-14]

Figure 1 shows the values of n_H (normalized to per Cu ion) for 4:3:3:4 doped with Tm. As in previous studies, the Hall signal is positive (holelike). (The values of n_H for $x=0$ are $\sim$20% larger than the single-crystal result of Takagi *et al.*[15] In an earlier report a lower value for n_H was obtained for a mixed phase Bi-Sr-Ca-Cu-O sample.[16]) As shown in Fig. 2, n_H (normalized to the cell volume $V=440$ Å^3) falls linearly with increasing x, intersecting the x axis at $x=1.37$. Near $x=0.1$, n_H shows an interesting cusp which is similar to that observed in Ni-doped 1:2:3. The magnitude of n_H (0.4/Cu ion) in the $x=0$ sample is also close to the hole density 0.5/Cu(2) inferred[17] for 1:2:3. We have also measured the resistivity (ρ) vs T for all the Hall samples. Samples with x between 0.0 and 1.0 are metallic, with ρ falling in the range of 1–10 mΩ cm. The samples with $x=1.5$ and 2.0 are approximately 100 times more resistive. Their resistivity is weakly T dependent above 150 K, but increases strongly below 100 K (in agreement with Ref. 11). For comparison, the variation of ρ vs x at 150 K is also shown in Fig. 2. The results show that as the chemical potential μ is raised (by increasing x), a relatively sharp metal-insulator transition occurs near $x=1.4$. Together, the two transport quantities show that transition is associated with a depletion of itinerant carriers.

The linear decrease of the Hall density n_H is reminiscent of the situation[5] in $La_{2-x}Sr_xCuO_4$ where n_H decreases linearly with decreasing x (Sr content) for x below

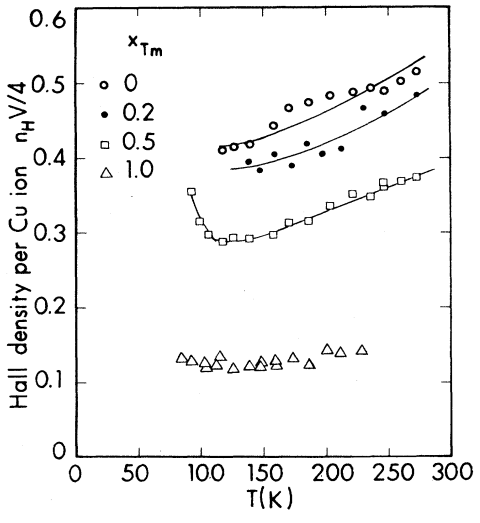

FIG. 1. Temperature dependence of the Hall carrier density per Cu ion, $n_HV/4$ ($V=440$ Å) for various x in $Bi_4Sr_3Ca_{3-x}Tm_xCu_4O_{16+y}$. The sharp upturn near 120 K in the $x=0.5$ sample may be caused by partial shorting of the Hall contacts due to superconducting fluctuations.

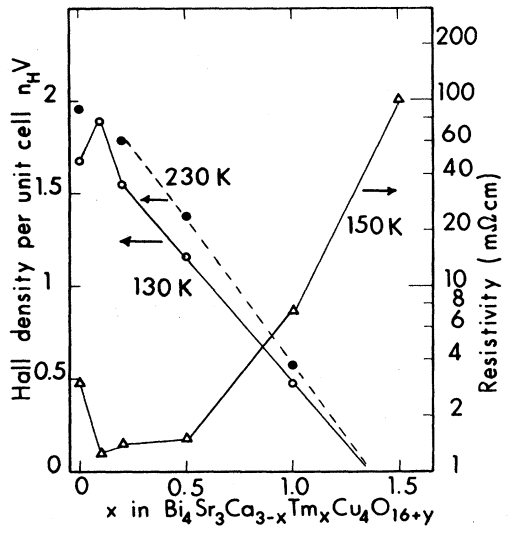

FIG. 2. The variation of the $n_H V$ (number of carriers per unit cell) in 4:3:3:4 with x at two temperatures: 130 K (open circles) and 230 K (filled circles). Note the decrease of the slope $d(n_H V)/dx$ as T decreases. Extrapolation of $n_H V$ locates the Mott-Hubbard gap edge at $x=1.37$. The polycrystalline resistivity ρ at 150 K (open triangles, plotted on log scale) increases almost by 100 between $x=0.5$ and 1.5.

0.15. This behavior provides strong evidence that the 4:3:3:4 compounds are in close proximity to a Mott-Hubbard insulating regime, in marked contrast to band-structure predictions. In the band structure reported by Mattheiss and Hamann[9] (MH) and by Herman, Kasowski, and Hsu[10] (HKH), the Fermi level is intersected by the two subbands formed from the familiar Cu $3d$-O $2p$ and the Bi $6p$-O $2p$ states. MH estimate the total carrier density to be 8.8×10^{21} cm^{-3}, with 10% of the carriers in the Bi $6p$-O $2p$ subband. Very low charge concentration is found at the Ca sites. Because of the overlap of the two subbands, the density of states (DOS) shows no gap between μ and the Bi $6p$ manifold which extends 4 eV above μ. We first analyze the Hall data using the $U=0$ band structure. Increasing x(Tm) from 0 to 1.5 in 4:3:3:4 implies that the electron population on the CuO_2 planes is increased by 0.4 per Cu ion. Assuming a bandwidth W of 3 eV for the Cu $3d$-O $2p$ band,[9] we infer that μ is raised by $W\delta/2\sim600$ mV. It is clear that within the $U=0$ picture such a relatively small shift in μ cannot result in insulating behavior. From the 3-eV width of the $3d$-$2p$ subband, and the strong overlap with the Bi $6p$-O $2p$ subband, we would predict that n_H should remain relatively unchanged as μ is raised by $W\delta/2$. In contrast, we observe a rapid linear decrease of n_H to very small densities. Thus, the Hall data provide strong evidence for a large gap approximately $W\delta/2$ in energy above μ in the 85-K system. The 100-fold jump in the resistivity between $x=0.5$ and 1.5 is also consistent with the existence of the Mott-Hubbard gap. (Results for R_H and ρ in the 4:4:2:4 phase doped with Tm, with $x=0.5$, 1.0, and 1.5 are broadly similar to the above.)

In analogy with the case of $La_{2-x}Sr_xCuO_4$ ($x<0.15$), we argue that the ground state of the Bi 2:2:1:2 system is a large-U Hubbard system. The Cu ions are all in the $3d^9$ state. Due to strong correlations, charge fluctuations are strongly suppressed;[18] the *strictly* stoichiometric compound $Bi_2(Sr,Ca)_3Cu_2O_8$ (without the Bi-O plane modulation) should be a good Mott-Hubbard insulator, despite the fact that μ is close to midband in the $U=0$ band structure. However, in the as-grown 4:3:3:4 compound (the $x=0$ sample) there already exists a significant density of itinerant holes, i.e., μ is lower than the Mott-Hubbard gap edge (see below). Nominally, the holes occupy states with mostly O $2p$ character.[19] Recent theoretical models[20] identify the carriers as a *singlet* bound state formed from a symmetric combination of O $2p\sigma$ and the Cu $3d_{x^2-y^2}$, referred to as $d^9\underline{L}$ (or formal Cu^{3+}). Substitution of Ca^{2+} with trivalent Tm raises the chemical potential. The ligand-hole population is steadily decreased as x increases until near $x=1.4$, the population is driven to zero, and μ is located within the Mott-Hubbard gap. From the resistivity data the system becomes insulating for $x>1.4$. The similarity with the case[5] of decreasing the Sr content in 2:1:4 ($x<0.15$) is quite close.

The argument above not only implies that the Cu $3d$-O $2p$ subband is split at midband by the Mott-Hubbard gap, but also requires that the Bi $6p$-O $2p$ subband *not* contain any current carrying states near μ. (Otherwise, neither the linear approach of n_H to zero nor the insulating behavior for $x>0$ would be observed.) This suggests that either the minimum of the Bi $6p$-O $2p$ subband is situated much higher than shown by the band-structure calculations, or that the states in the Bi-O plane are *strongly* localized. In this case the Bi-O planes act as an electron reservoir similar to the Cu(1) chains[6] in 1:2:3. As x increases, the fraction of holes in the Cu-O planes is decreased while the localized holes in the Bi-O planes increase. However, the latter do not affect the Hall signal, which measures only the itinerant carriers. A discussion of whether the Bi $6p$-O $2p$ subband intersects μ has also been given by Sleight.[21]

The variation of T_c with Tm content (shown in Fig. 3) shows the surprising nonlinear trend previously reported in Ref. 11. Rather than decreasing linearly with x, T_c shows a slight initial increase (~4 K) and then stays roughly constant until x exceeds 0.5. Beyond 0.5, T_c decreases rapidly, becoming zero in the $x=1.5$ sample. On the basis of the Hall data in the range $0<x<0.5$, we adopt the viewpoint that the plateau in T_c occurs *despite* a significant change in n (see Ref. 11 for an alternate view). A similar plateau at 40 K is well known in the 2:1:4 system.[8] Interestingly, T_c is actually lower (and ρ higher) in the $x=0$ sample compared with the $x=0.1$ and 0.2 samples, i.e., carrier scattering is more severe in the $x=0$ sample. This is brought out by plotting the polycrystalline Hall mobility μ_H ($=R_H/\rho$) vs x in Fig. 3 (filled circles). The rather severe reduction in μ_H as x approaches 0 suggests that the carriers in undoped 4:3:3:4 undergo more scattering than in the lightly doped samples. These results can be accounted for by assuming that the strong incommensurate modulation[22] in the Bi-O planes leads to defects which strongly scatter the carriers in the CuO_2 planes. Substitution of Ca with Tm at the sites between

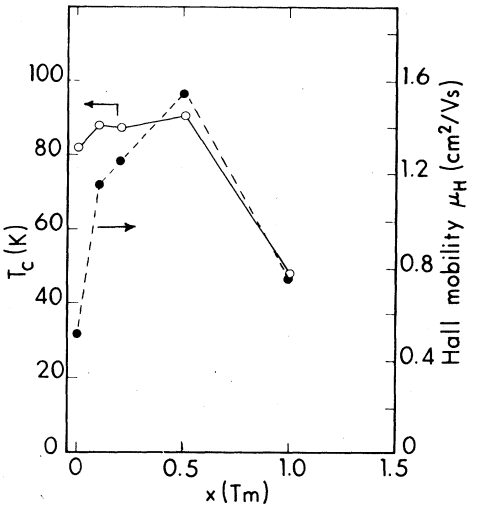

FIG. 3. Variation of the transition temperature T_c vs x (open circles) compared with the polycrystalline Hall mobility μ_H at 150 K (filled circles) for Tm-doped 4:3:3:4 (T_c for the $x=1.5$ and 2.0 samples is zero.) The decrease in both quantities as x approaches 0 suggests increased lattice-defect scattering in the $x=0$ sample.

the CuO_2 planes apparently helps to relieve the strain and reduce the defect density. This leads to an improvement in μ_H and a slight enhancement of T_c. At large x, the improvement in μ_H entails the cost of carrier reduction (as shown in Fig. 2) so that T_c eventually decreases. The nonmonotonic variation of T_c with x indicates that in addition to n, scattering mechanisms acting within the CuO_2 planes may have a significant inhibitive effect on T_c in the high-T_c oxides, as suggested by the Ni-doping studies[17,23] on 1:2:3 and 2:1:4.

In Ref. 23, which analyzes the T dependence of n_H in 2:1:4 and 1:2:3, it was shown that whenever T_c is suppressed by creating in-plane disorder (substituting Cu with Ni), or by depleting n (substituting with Co), the slope dn_H/dT is systematically suppressed as well. The results in Fig. 1 show that a similar trend also prevails for the Bi system. Whereas in the $x=0$, 0.2, 0.5 samples n_H increases with T (although not as strongly as in 1:2:3), the T dependence of n_H is negligible in the $x=1$ sample where T_c has been depressed to 50 K. The decrease in the T dependence of n_H (as T_c is suppressed) results in the characteristic "converging" pattern of the n_H vs x curves at different T's in Fig. 2. Such converging profiles were previously found[23] in 1:2:3 (doped with Co and Ni) and in Ni doped 2:1:4. In Fig. 2, the slope $d(n_H V)/dx$ at large x systematically changes from -1.60 (at 230 K) to -1.30 (at 130 K). This strongly suggests that the slope may approach the value -1.0 (consistent with each Tm donating one excess electron to the CuO_2 planes) at sufficiently low T.

We next consider the source of the holes in the $x=0$ sample. Direct charge balance in $Bi_4Sr_3Ca_{3-x}Tm_xCu_4O_{16+y}$ implies that the filling factor δ equals $(2y-x)/4$. For the $x=0$ sample, TGA measurements[11] yield $y=0.25$–0.30, corresponding to $\delta_{TGA}=0.125$–0.15. A higher value for $y=0.42$ (implying $\delta=0.21$) has been obtained in another study[24] which compares Bi 2:2:1:2 with the new isostructural compound $Bi_{10}Sr_{15}Fe_{10}O_{46}$. These numbers are significantly lower than the $\delta(0.4)$ derived from the Hall data. Although further work is required to resolve the discrepancy, we note that the linear extrapolation of n_H to zero implies that the Mott-Hubbard edge is at $x=1.4$ which is close to the value 1.6 computed from 4δ, i.e., the Hall data appear to be tracking the carrier population fairly closely. The charge balance estimate is sensitive to very slight Bi or Sr deficiencies. (For example, if 1 out of 16 Bi atoms is missing in the $x=0$ sample, our value for δ would be consistent with the value of $y=0.42$ given in Ref. 24.) In view of the incommensurate modulation of the Bi-O plane[21] such slight deficiencies in Bi or Sr cannot be excluded. The TGA results[11] also show that y increases roughly linearly from 0.25 (at $x=0$) at ~ 1.2 (at $x=2.0$). The large change in anion charge is also difficult to reconcile with the Hall data.

In summary, Hall measurements on Bi 2:2:1:2 show that the hole density (0.4/Cu) is close to that found[17] in 1:2:3 [0.5/Cu(2)]. The removal of these holes by Tm doping drives the system insulating, in sharp contrast to band-structure predictions. Thus, we believe that Bi 2:2:1:2 is a strongly correlated Mott-Hubbard system, with a behavior remarkably similar to 2:1:4. The significant density of holes in the undoped compound is possibly due to oxygen excess or deficiency in Sr and Bi. Rather than being linear in n, T_c vs x exhibits a broad plateau peaking at 85 K. The variation of the Hall mobility with x suggests that the undoped compound may have severe lattice strain. We also discussed the implications for the existence of a large overlap at μ between subbands formed from Cu $3d$–O $2p$ and Bi $6p$–O $2p$ states.

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