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Carrier-density-related superconductivity in bismuth cuprates

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We report Hall-constant (R_H) measurements on the Bi-Sr-Ca-Cu-O system. Two systems, 2:2:1:2 and 2:2:2:3, have been studied with a variety of heat treatments and cationic substitutions (Pb, Gd, Nd, Sm). The carrier density ($n=1/eR_H$) at 300 K as a function of T_c for these polycrystalline samples show two distinct maxima—one corresponding to the low-T_c (2:2:1:2) phase and the other to the high-T_c (2:2:2:3) phase. The data point to compelling evidence of correlations between charge carriers and superconductivity confirming similar Hall data on Y- and La-based cuprates. A discussion of some relevant models is presented.

Ever since the discovery of high-temperature superconductivity in copper-based oxides with a perovskitelike structure, several attempts have been made to establish a relation between normal-state and superconducting properties. It was thus shown that the carrier density $n=1/eR_H$ (R_H:Hall constant) is strongly related to the superconducting transition temperature T_c in $La_{2-x}Sr_xCuO_4$ (Ref. 1) and in $YBa_2Cu_3O_{7-y}$ (Ref. 2). With increasing n, T_c increases, takes a maximum, and then decreases as n increases further. In addition, $1/eR_H$ decreases linearly with temperature as does the resistivity for $T>T_c$. These observations pose severe restrictions, if not challenges, to any theoretical model being proposed to explain high-temperature superconductivity in these systems. Recently, a relation between n and T_c was also shown to exist in $Bi_2Sr_2CaCu_2O_y$ (2:2:1:2) system.[3,4] We wish to report here on the Hall data of several compounds of the 2:2:1:2 and 2:2:2:3 of Bi systems. Different substitutions (Pb, Nd, Sm, Gd, Hg) and heat treatments have been used in order to vary T_c, enabling us to investigate the influence of n on T_c. In addition, R_H has been measured as a function of T for a 107-K superconductor. Our studies, though on polycrystalline samples, seem to reinforce the earlier conclusions[1,2] that there is a definite relation between the carrier (hole) density and the occurrence of the superconductivity. Finally, an attempt has been made to analyze these results with the help of some of the theoretical models.

The ceramic samples in pellet form, used in this study, have been prepared by standard solid-state sintering techniques, starting from high-purity oxides or carbonates. Care was taken to grind the samples at least twice after calcination. A Cu $K\alpha_1$ aligned Guinier camera was used to determine the structure by x-ray analyses. Twenty to thirty reflections were used to calculate the lattice parameters. For each reflection, the rms standard deviation in 2θ is less than 4×10^{-2} degree.

The low-T_c 2:2:1:2 structure is characterized by $a=b=5.4$ Å and $c=30.8$ Å whereas the high-T_c 2:2:2:3 structure has a c parameter of 37.1 Å. In the case of 2:2:2:3 samples, the ratio of the x-ray intensity of the (00ξ) peak was used to estimate the high-T_c phase. Indium was ultrasonically welded to the samples to obtain Ohmic contacts. Standard ac techniques were used to measure the resistivity ρ and R_H as a function of temperature. The measuring current was 10 mA and the magnetic field was 1 T. T_c is the temperature at which ρ lies in the range of 0.5 to 1×10^{-6} Ω cm. Table I summarizes the nominal composition, heat treatment, structural data, and T_c of the samples we have studied. No extra ray (Gd_2O_3, Sm_2O_3, PbO, ...) was detected. The unit-cell parameters of the 2:2:1:2 or 2:2:2:3 structure have not shown a significant variation with any substituted rare earth (up to 20% of the dopants). We first discuss the temperature dependence of R_H of the high-T_c phase before presenting the 300-K data of the rest. R_H as a function of T for a high-T_c ($T_c=107$ K) sample is shown in Fig. 1. This sample with 20% Pb is estimated to contain about 75% of the high-T_c phase. The conductivity is p type and R_H obeys the $1/T$ law. It was recently shown that the value of R_H at 300 K and its temperature variation is strongly affected by the preparation conditions.[5] However, even for the purest 2:2:2:3 with Pb sample as claimed by Maeda *et al.*,[5] R_H does increase as T decreases. R_H of our sample is about twice that observed (for sample *B*) by Maeda *et al.* The transport data obtained on polycrystals are influenced by porosity and grain boundaries. However, it was pointed out recently that R_H and ρ in polycrystals can be converted to corresponding (a,b) plane values by multiplicative correction factors.[6,7] In the case of $YBa_2Cu_3O_7$, the polycrystalline data after correction agreed with those obtained in single crystals.[8] We do not attempt here to make any such corrections, but simply point out such a possibility.

Several models have been proposed[9,10] to explain the temperature dependence of R_H in high-T_c materials. We will comment briefly on some of the models. Since R_H does not vary as susceptibility, the conventional magnetic skew scattering cannot describe the present data as was suggested earlier[8] in the case of $YBa_2Cu_3O_7$. If one assumes the presence of both holes and electrons in these oxides, an expression for R_H can be worked out in a two-band model in low fields. Indeed, one does observe in $YBa_2Cu_3O_7$, for $H\|(a,b)$, a negative Hall coefficient. Thus, several groups have used some variations or others of a two-band model and successfully analyzed the Hall

TABLE I. Nominal composition, heat treatment, superconducting transition temperatures, and carrier density of bismuth cuprates with different substitutions. SC1 denotes slow cooling 25 °C/h; SC2 denotes slow cooling 100 °C/h; q denotes quench in ambient air; a denotes air; O denotes oxygen.

Starting composition	Final heat treatment (°C)	T_c (K) ($R=0$)	n (300 K) (10^{21} cm^{-3})	Structure 2:2:2:3	2:2:1:2
2:2:2:3+20% Pb	850°/a 150 h+SC1	105	1.25	65%	35%
2:2:2:3+20% Pb	850°/a 200 h+SC1	107	1.70	75%	25%
2:2:2:3+20% Pb	855°/a 100 h+SC1	103	2.10	50%	50%
2:2:2:3+20% Pb	850°/a 80 h+SC2	101	2.50	20%	80%
2:2:2:3+20% Pb	845°/a 80 h+SC2	97	2.65	5%	95%
2:2:2:3+20% Pb	840°/a 80 h+SC2	93	2.75	5%	95%
2:2:2:3+20% Pb+0.5% Gd	855°/a 80 h+SC1	101	2.55	25%	75%
2:2:2:4[a]+20% Sm	860°/a 48 h+SC2	46	1.70		2:2:1:2
2:2:2:3[a]+10% Sm	840°/a +q	62	2.20		2:2:1:2
2:2:2:3[a]+10% Sm	860°/a +500°/O 48 h+q	67	2.90		2:2:1:2
2:2:2:4[a]+20% Pb	850°/a 48 h+SC2	63	2.85		2:2:1:2
2:2:2:3[a]+20% Pb+0.5% Gd	855°/a 24 h+SC2	62	3.50		2:2:1:2
2:2:2:4[a]	865°/a 24 h+SC2	65	2.10		2:2:1:2
2:2:2:3[a]+20% Pb+1.25% Gd	855°/a 60 h+SC2	65	4.70		2:2:1:2
2:2:2:3[a]+10% Hg	845°/a 80 h+SC1	59	4.80		2:2:1:2
2:2:2:3[a]	840°/a +SC2	59	4.95		2:2:1:2
2:2:1:2+10% Nd	860°/a +500°/O 48 h+q	57	5.40		2:2:1:2

[a]Compounds with excess of Cu or Ca compared to the precipitated phases.

data. However, these models have certain starting assumptions (like $n=p$) which need not be true as was also pointed out recently.[11] Another qualitative explanation is based on the fact that these are two-dimensional materials and the temperature variation of R_H is a result of the strong anisotropic character. Finally, it was proposed[11] that this anomalous behavior may arise from an asymmetric scattering mechanism (as yet unknown) and which is specific to the particular ground state of these oxides. The argument was based on the fact that the linear temperature dependence of R_H is strongly modified in $YBa_2Cu_{3-x}Co_xO_{7-y}$, as x increases, accompanied by a decrease in T_c, implying an absence of the linear temperature dependence of R_H for nonsuperconducting samples. However, Ando *et al.*[12] have observed a linear temperature dependence of R_H in a nonsuperconductor $La_2SrCu_2O_y$. This could be an exception, and if so, needs to be verified in other nonsuperconducting two-dimensional copper-oxide-based systems.

We now discuss the Hall data at 300 K of the samples listed in Table I. The hole density taken as $1/eR_H$ is plotted in Fig. 2, as a function of T_c. Our samples fall into two curves well separated from each other. The lower branch reflects the low-T_c phase (80 K) and the higher branch the 100-K high-T_c phase. Each branch is characterized by a distinct maximum. In both the systems, T_c increases as n increases, though it is easier to see this in the 2:2:1:2 systems mostly because of a larger number of samples prepared under different conditions and with different substitutions. A similar variation of T_c as n is

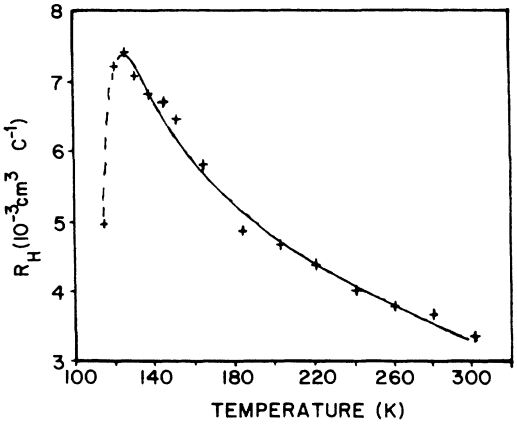

FIG. 1. Hall constant as a function of temperature of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_y$.

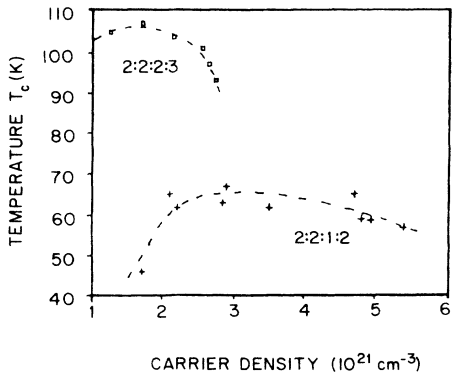

FIG. 2. Carrier density ($1/eR_H$) at 300 K as a function of superconducting transition temperatures for the samples described in Table I.

varied was shown recently[3] in the case of the Bi 2:2:1:2 system substituted with different cations (mono and trivalent) at the Sr and Ca sites. Our maximum in T_c (for the lower part of the curve) is lower compared to the maximum reported in Ref. 3 mainly because of two reasons: Our samples contain an excess of Cu and the heat treatment procedures are different. What seems to be important is whatever may be the method of changing T_c—by heat treatment or by substitutions—a maximum in T_c is observed as n increases.

It is interesting to compare our findings with those obtained by an entirely different contactless technique, namely muon spin resonance.[13] Using this technique, the spin relaxation rate which is proportional to n_s/m^* (n_s is the number of superconducting electrons and m^* the effective mass) was measured as a function of T_c for sixteen different specimens including the $La_{2-x}Sr_xCuO_4$, Y, Bi, and Tl systems. For all these systems, as n_s/m^* increase, T_c increases, shows a maximum, and then decreases for any further increase in n_s/m^*, though very few data points are reported for the Bi 2:2:2:3 system. In the absence of a direct measurement of m^*, a direct comparison with our data is difficult. However, these two findings do bring an important result, namely, the carrier concentration is directly related to T_c.

As noted earlier,[3] such a linear relation between n and T_c cannot be expected in the weak-coupling limit of the BCS theory of superconductivity. In two dimensions,[14] however, with an attraction V between carriers within a cutoff energy $\hbar\omega$ of the Fermi energy and a constant density of states, N,

$$T_c(\hbar\omega)^{1/2}E_F^{1/2}\exp(-1/NV)n^{1/2} \propto \exp(-1/NV)$$

for hole Fermi energies $E_F < \hbar\omega$, but is simply proportional to $\exp(-1/NV)$ for $E_F > \hbar\omega$. If one assumes that V involves Coulomb interactions of some kind and thus decreases as k_F ($\propto n^{1/2}$) increases, then one finds a maximum in T_c whose sharpness depends on the part of the curve where the transition from $E_F < \hbar\omega$ to $E_F > \hbar\omega$ occurs. If the energy gap becomes comparable with the Fermi energy, then the situation becomes more complicated.[14] Further, it was recently pointed out[15] that in two dimensions, for any coupling which can give a two-body bound state, a state intermediate between a Cooper-paired state and a Bose-condensed state of tightly bound pairs may arise.

Yet another qualitative description is provided by the bipolaron model[16–19] which is briefly described as follows. At low carrier densities, in these two-dimensional materials with a high ratio of static to high frequency dielectric constant, the conditions are favorable for bipolarons to form and condense at relatively high temperatures. As n increases, T_c increases. However, for any further increase in n, the bipolarons loose stability resulting in a decrease of T_c. This model also accounts for the increase in T_c as the number of Cu-O layers increases. However, the observed large susceptibility at $T > T_c$ and the assumption that $m^* = 20\ m_e$, are difficult to justify as yet in this model. One should also note that an attempt was made long ago to point out the importance of hole conductivity in various conventional superconductors.[20,21] More recently, a model has been proposed[22] which accounts qualitatively for the increase in T_c as n increases. This model, however, seems to imply that even in the newly discovered[23] superconductor $Nd_{2-x}Ce_xCuO_{4-y}$—which shows n-type conductivity by Hall effect measurements—the mobile carriers are holes and not electrons. Further studies are necessary to clarify this point.

In conclusion, our extensive Hall data in the Bi 2:2:2:3 and 2:2:1:2 systems with varying substitutions and heat treatments point to a compelling evidence of correlations between charge carriers and the superconducting transition temperature. Our studies confirm earlier findings on other systems such as $La_{2-x}Sr_xCuO_4$ (Ref. 1) and $YBa_2Cu_{3-x}M_xO_{7-y}$ [M=Co (Ref. 11), M=Fe (Ref. 24)] and further support the results obtained by a noncontact technique, i.e., muon spin resonance.

Though the two main results—namely the linear temperature dependence of $1/eR_H$ and the n-T_c relation with maxima distinct for the three Cu-O-based superconductors—should be verified on single crystals, these studies, we believe nevertheless, should provide stimulating starting points for any model to account for the observed superconductivity.

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[1]N. P. Ong, Z. Z. Wang, J. Clayhold, J. M. Tarascon, L. H. Greene, and W. R. McKinnon, Phys. Rev. B **35**, 8807 (1987); S. Uchida, M. Takagi, H. Ishii, M. Eisaki, T. Yake, S. Tajima, and S. Tanaka, Jpn. J. Appl. Phys. **26**, L445 (1987); J. B. Torrance, Y. Tokura, A. I. Nazzal, A. Bezinge, T. C. Huang, and S. S. Parkin, Phys. Rev. Lett. **61**, 1127 (1988).

[2]M. W. Shafer, T. Penney, B. L. Olsen, R. L. Greene, and R. H. Koch, Phys. Rev. B **39**, 2914 (1989); Y. Tokura, J. B. Torrance, T. C. Huang, and A. I. Nazzal, *ibid.* **38**, 7156 (1988).

[3]Y. Koike, Y. Iwabuchi, S. Hosoya, N. Kobayashi, and T. Fukase, Physica C **159**, 105 (1989).

[4]M. Rateau, R. Suryanarayanan, O. Gorochov, and H. Pankowska, Physica C (to be published).

[5]A. Maeda, K. Noda, K. Uchinokura, and S. Tanaka, Jpn. J. Appl. Phys. **28**, L576 (1989).

[6]G. S. Grader, P. K. Gallagher, and A. T. Fiory, Phys. Rev. B **38**, 844 (1988).

[7]T. K. Xia and D. Stroud, Phys. Rev. B **37**, 118 (1988).

[8]A. T. Fiory and G. S. Grader, Phys. Rev. B **38**, 9198 (1988).

[9]T. Penney, S. von Molnar, D. Kaiser, F. Holtzberg, and A. W. Kleinsasser, Phys. Rev. B **38**, 2918 (1988).

[10]C. Uher and A. B. Kaiser, Phys. Lett. A **125**, 421 (1987); A. Davidson, P. Santhanam, A. Palerski, and M. J. Brady, Phys. Rev. B **38**, 2828 (1988); D. Y. Xing and C. S. Tang, *ibid.* **38**, 5134 (1988); D. M. Eagles, Solid State Commun. **69**, 229 (1989), and references therein.

[11]J. Clayhold, N. P. Ong, Z. Z. Wang, J. M. Tarascon, and P. Barboux, Phys. Rev. B **39**, 7324 (1989).

[12]Y. Ando, M. Sera, S. Yamagata, S. Kondohm, M. Onoda, and M. Sato, Solid State Commun. **70**, 303 (1989).

[13]Y. J. Uemura *et al.*, Phys. Rev. Lett. **62**, 2317 (1989), and references therein.

[14]D. M. Eagles, Physica C **158**, 258 (1989); Phys. Rev. **164**, 489

(1967); *ibid.* **186**, 456 (1969).
[15]M. Randeria, J. M. Duan, and L. Y. Shieh, Phys. Rev. Lett. **62**, 981 (1989).
[16]M. R. Schaffroth, Phys. Rev. **100**, 463 (1955).
[17]A. S. Alexandrov and J. Ranninger, Phys. Rev. B **24**, 1164 (1981); **33**, 4526 (1986).
[18]B. K. Chakraverty, J. Phys. (Paris) **49**, 99 (1979).
[19]D. Emin and M. S. Hillery, Phys. Rev. B **39**, 6575 (1989); D. Emin, Phys. Rev. Lett. **62**, 1544 (1989).
[20]I. Kiokin and B. Lazarev, Zh. Eksp. Teor. Fiz. **3**, 44 (1933).
[21]I. M. Chapnik, Dokl. Akad. Nauk SSSR **141**, 70 (1962) [Sov. Phys. Dokl. **6**, 988 (1962)]; Phys. Lett. **A72**, 255 (1979).
[22]J. E. Hirsch and S. Tang, Phys. Rev. B **40**, 2179 (1989); J. E. Hirsch, Physica C **158**, 326 (1989).
[23]Y. Tokura, H. Takagi, and S. Uchida, Nature (London) **337**, 345 (1989); H. Takagi, S. Uchida, and Y. Tokura, Phys. Rev. Lett. **62**, 1197 (1989).
[24]G. Priftis, A. Ghorayeb, O. Gorochov, R. Suryanarayanan, H. Pankowska, and M. Rateau, Physica C (to be published).