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Carrier density correlation with superconductivity—A universal law?

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Abstract. Hall constants (R_H) at 300 K of three families of CuO-based superconductors are presented—the 123 YBaCuO with Fe substitution, the 2212 and 2223 Bi systems with Pb, Gd, Nd, Sm substitutions. In all these systems, R_H is positive indicating hole conductivity. T_c increases initially as the hole density ($p = 1/R_H e$) increases and shows a maximum. Each family shows a maximum value of T_c but at different values of p. These data along with the observation of n-type conductivity in NdCeCuO are discussed in the light of certain models.

Keywords. Hole conductivity; Hall constant; bismuth cuprates; iron-substituted YBaCuO; n-type; bi-polaron; Hirsch model.

1. Introduction

Soon after the discovery of high temperature superconductivity in cuprates, Hall constant (R_H) measurements have shown in the case of $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_y$ that the holes (p) are the majority carriers and T_c increases initially as p increases (Ong *et al* 1987; Uchida *et al* 1987; Shafer *et al* 1987, 1989; Torrance *et al* 1988; Tokura *et al* 1988; Penney *et al* 1988). It is important to extend these studies to other superconductors and to see if similar relation could be established. We would like to focus our attention on four different systems—$YBa_2Cu_{3-x}Fe_xO_{7-y}$ ($0 < x < 0{\cdot}15$) (YBCO), $Bi_2Sr_2Ca_1Cu_2O_y$ (2212), $Bi_2Sr_2Ca_2Cu_3O_y$ (2223), and $Nd_{1{\cdot}85}Ce_{0{\cdot}15}CuO_{4-y}$ (NCCO).

2. Experimental techniques

The ceramic samples used in the present study were prepared by standard solid-state sintering. For details see Suryanarayanan *et al* (1989a,b). $CuK_{\alpha 1}$-aligned Guinier camera was used for X-ray analyses. For each sample, about 20 to 30 reflections were measured to calculate the lattice parameters. The deviation between the calculated and experimental values of 2θ was typically less than $4{\cdot}10^{-2}$. Indium was ultrasonically welded at six points on the sample to make electrical contacts. Standard a.c. technique was used to measure the resistivity as a function of temperature. The Hall voltage was measured by passing a current of 1 to 10 mA in a magnetic field of 1·1 tesla.

3. Results and discussion

3.1 $YBa_2Cu_{3-x}Fe_xO_{7-y}$

For $0 < x < 0{\cdot}07$, the lattice parameters a and b increase and the orthorhombicity is almost constant. For $0{\cdot}07 < x < 0{\cdot}10$, there is a strong decrease in the orthorhombicity

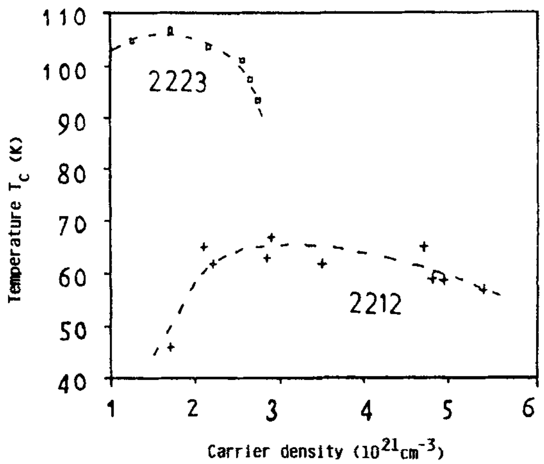

Figure 1. T_c as a function of hole density ($1/R_He$) for the bismuth cuprates described in table 1.

and in this range of composition, the diffraction lines broaden and it is impossible to detect the presence of two phase regions (for details see Priftis *et al* 1989). It was shown earlier that T_c does not change as we go through this transformation if the samples are cooled slowly (Tarascon *et al* 1988; Suryanarayanan *et al* 1989a).

All these samples indicate p-type conductivity as shown by the Hall effect measurements. The relation between T_c and $p = 1/R_He$ (using a single-band model) is shown in figure 1. In addition to the data points (taken at 300 K) corresponding to Fe samples three data points on undoped samples obtained by quenching these from different temperatures are also shown. Thus, $T_c = 20$ K was measured for an undoped sample quenched from 650 C in air. First, we note that as p increases slowly, T_c increases quickly and reaches a plateau for $p = 5 \times 10^{21}\,\mathrm{cm}^{-3}$. Further, the data points of undoped samples having a different oxygen stoichiometry fall on the same curve as do the doped samples. This indicates an important point, namely, irrespective of the way in which we vary the carrier concentration (by deviations from oxygen stoichiometry or by introducing Fe impurities), there seems to be only one relation between p and T_c. This increase in T_c as p increases is also observed for the data taken at 100 K for the doped samples (figure 1).

3.2 *Bismuth cuprates*

The different samples used in this study along with the heat treatment, T_c values, the carrier density at 300 K and the structural data are summarized in table 1. All the samples studied here without exception show p-type conductivity. The hole density ($1/R_He$) of these samples is plotted as a $f(T)$ in figure 2. Our samples fall into two curves well separated from each other. The lower branch reflects the low T_c (2212) phase and the higher branch the 100 K the high T_c (2223) phase. Each branch is characterized by a distinct maximum. In both systems, T_c increases as p increases very similarly to the Fe-doped YBCO samples discussed above. Similar results were reported recently for the (2212) system, though obtained using different cationic substitutions (Koike *et al* 1989).

Table 1. Nominal composition, heat treatment. superconducting transition temperatures, and carrier density of bismuth cuprates with different substitution. SCl 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.

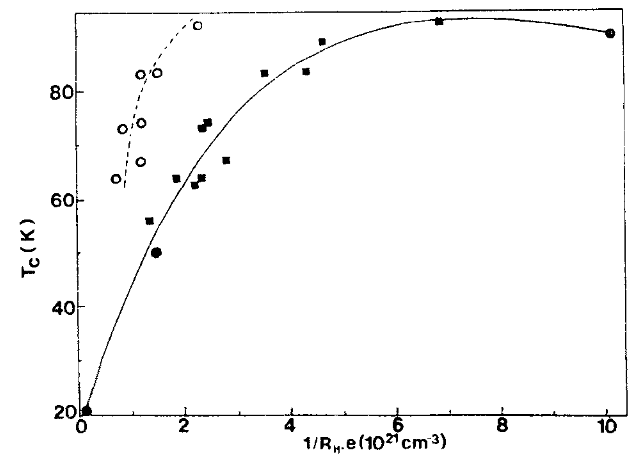

Figure 2. T_c as a function of hole density ($1/R_H e$) of $YBa_2Cu_{3-x}Fe_xO_{7-y}$ at 300 K (■) and at 100 K (○); (●) for $x = 0$.

3.3 *NCCO*

Contrary to the above materials, this system shows n-type conductivity as pointed out earlier (Tokura *et al* 1989; Takagi *et al* 1989) and confirmed by us (Suryanarayanan *et al* 1989b). Substitutional studies in this system have not been done but will be very interesting.

It is noteworthy to compare our findings with those obtained by an entirely different technique, namely, muon spin relaxation (Uemura *et al* 1989). The muon spin relaxation rate which is proportional to n_s/m^* (n_s = number of superconducting electrons and m^* = effective mass) has been measured for sixteen different specimens including $La_{2-x}Sr_2CuO_4$, Y, Bi and Tl systems. For all these systems, as n_s/m^* increases, T_c increases, shows a maximum and then decreases for any further increase in n_s/m^*. In the absence of a direct measurement of m^*, a direct comparison with our data is difficult. However, a striking resemblance between this and our data cannot be ignored. No such studies have been reported as yet on NCCO (n-type) system.

In what follows, a brief attempt is made to understand qualitatively these results. A linear relation between p and T_c cannot be expected in the weak-coupling limit of the BCS theory of superconductivity (for details see Eagles 1967, 1969 and 1989; Randeria *et al* 1989). It is interesting to look at the qualitative description provided by the bi-polaron model (Alexandrov and Ranninger 1981; Chakraverty 1979; Emin 1989). At low carrier densities in these two-dimensional materials with a high ratio of static-to-high frequency dielectric constant, this model foresees conditions favourable for the formation and a condensation of bi-polarons at relatively high temperatures. As p increases, T_c would increase. However, for any further increase in p, the bi-polarons loose stability resulting in a decrease of T_c. On the other hand, the observed large susceptibility at $T > T_c$ (in the undoped samples) and the assumption that $m^* = 20\, m_e$ are difficult to justify as yet in this model.

One should note that an attempt was made long ago to point out the importance of the hole conductivity in various conventional superconductors (Kiokin and Lazarev 1933; Chapnik 1962, 1979). For example, in the case of the solid solution Cr–V–Ti, T_c

increases with the hole concentration, reaches a plateau and then decreases (Hulm and Blaughter 1961). More recently a model has been proposed which accounts qualitatively for the increase in T_c as p increases (Hirsch 1989). This model, however, seems to imply that even in the newly discovered superconductor $Nd_{2-x}Ce_xCuO_{4-y}$, mobile carriers are holes and not electrons, whereas Hall effect measurements indicate n-type conductivity. Preliminary results indicate that n-type conductivity is not confined to NCCO system. Thus, Hall constant measurements done in our laboratory seem to indicate n-type conductivity in Tl-Ce (Th)–Ba–Cu–O system (Subba Rao *et al* to be published). Further theoretical and experimental studies of other superconductors in which mobile carriers are electrons are necessary to clarify this view point.

4. Conclusions

Our data, not withstanding the polycrystalline nature of the samples, bring forth an important characteristic of the cuprate superconductors—the influence of carrier density on T_c—that is difficult to explain quantitatively by the existing theoretical models. Extension of this work to other cuprates in which the mobile carriers are suspected to be electrons should help progress further understanding of the mechanism of high temperature superconductivity and may possibly indicate if the behaviour described here is universal.

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