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Electrical transport and superconductivity in the $(Y_{0.8}Ca_{0.2})Ba_2Cu_3O_y$ system with variable oxygen content

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The effect of oxygen content and thermal treatment has been studied in the $(Y_{0.8}Ca_{0.2})Ba_2Cu_3O_y$ system. The introduction of Ca altered the normal state and superconducting properties substantially. Particularly intriguing is that Ca-doped samples with more oxygen-vacancy disorder have higher superconducting transition temperatures (T_c) and lower resistivities, contrary to the non-Ca-doped system. The correlation between T_c and carrier concentration cannot be described by the empirical relation observed in many high-T_c oxides.

1. Introduction

The effect of oxygen stoichiometry in the $YBa_2Cu_3O_{7-\delta}$ (YBCO) superconductor has been extensively studied [1,2]. It is now agreed upon that the superconducting transition temperature T_c depends on the mobile carrier concentration, n, in the $Cu–O_2$ plane. The oxygen content controls n in a non-linear fashion [1,2] because carriers are distributed both in the planes and in the Cu–O chains. In addition to varying the oxygen content, cation doping [3–12], e.g., at the Y site, may also change n and affect many properties accordingly. These two methods, though similar in terms of charge counting, may differ in many ways in affecting the normal state and superconducting properties. It is worthwhile to understand how the electronic states are influenced by these two doping schemes.

Among all cation dopings, Ca substitution for Y in $YBa_2Cu_3O_{7-\delta}$ has received much attention [2,4–12]. The valence state of Ca^{2+} is lower than that of Y^{3+}; such a substitution will increase n. Hole doping due to Ca is well documented. For example, Ca-doping is able to revive the superconductivity (to $T_c \sim 40$ K) of $PrBa_2Cu_3O_{7-\delta}$ which is a semiconductor [5]. Also, the introduction of Ca will increase T_c from 0 K to about 52 K in $YBa_2Cu_{2.55}Co_{0.45}O_{7-\delta}$ [6]. Here, Ca increases the carrier number and counter-balances the effect of Co^{3+} which goes into the Cu–O chain site and is hole filling. The effect of Ca-doping in pure YBCO has also been studied [2,7–12]. Again, Ca is able to increase T_c of the oxygen deficient and tetragonal YBCO samples. In the fully-oxygenated YBCO, however, Ca-doping (above 6%) is accompanied by a reduction in oxygen content [8,11]. Therefore, the excess carriers introduced tend to be counter-balanced by hole filling. The important issue here is whether the carriers supplied by Ca and by O play a similar role in the superconducting properties.

To date, studies involving Ca-doping have yielded useful information about the role of the carrier concentration and its type in the normal state and in the superconducting properties [2,4–12]. Nevertheless, a systematic study is lacking that deals with Ca-doped YBCO samples with a wide range of oxygen content and of thermal treatment. Investigation of T_c correlation with normal state properties is also needed in this area.

We have prepared a series of $(Y_{0.8}Ca_{0.2})Ba_2Cu_3O_y$ samples with a large variable oxygen content. These samples were also treated in different thermal conditions, and therefore have different oxygen-vacancy orders. We found that Ca-doping profoundly changes the well known T_c versus δ relation in pure YBCO. Most dramatically, quenched Ca-doped YBCO sam-

ples have a higher T_c than slowly-cooled samples. Based on a Hall effect measurement, we also found that the empirical relation between T_c and the carrier concentration, widely seen in many high-T_c oxides, becomes largely invalid in Ca-doped YBCO. These observations reveal that Ca plays a much more interesting role than just that of a carrier provider in YBCO.

2. Experimental

The samples were made using the standard solid-state reaction method. We first prepared a batch of fully-oxygenated $(Y_{0.8}Ca_{0.2})Ba_2Cu_3O_y$ powders that were annealed in an oxygen atmosphere at $T=940°C$ for over 100 h with two intermediate grindings. The powders, checked by X-ray analysis, had a single phase with an impurity level less than 2%. The pellets, made from the powders, were cut into slices with dimensions of about $\sim 10\times3\times0.3$ mm^3 for electrical measurements.

The oxygen content of a sample was varied by annealing at a specific T in flowing Ar gas. It is well known that the oxygen-vacancy order and electrical properties of YBCO depend on the thermal history. We prepared our samples using two different routes. At first, a sample was heated up to a predetermined T in Ar gas and kept there for at least 12 h. For the first group, referred to as annealed samples, we cooled the samples slowly ($\sim 5°$/min) back to room temperature. In the second group, the samples were quenched in liquid nitrogen, and are therefore called quenched samples. They are metastable in nature and retain their structure at high T. The oxygen stoichiometry for a fully-oxygenated pure YBCO is known to be about 6.96 [3,10,11], slightly below the ideal number of 7. Ca-doping below 6% has little effect on the oxygen content [10]. However, a higher level of Ca-doping will reduce the oxygen content. It was found that 20% Ca-doping brings the oxygen stoichiometry to about 6.85 [8,11]. Therefore,the excess carriers due to Ca tend to be compensated by the oxygen vacancies. From now on, whenever we use oxygen deficiency δ to specify a sample, we refer to the initial oxygen stoichiometry of 6.85. Figure 1 shows the oxygen deficiency, determined by thermogravity measurement, as a function of the annealing temperature for both groups of samples.

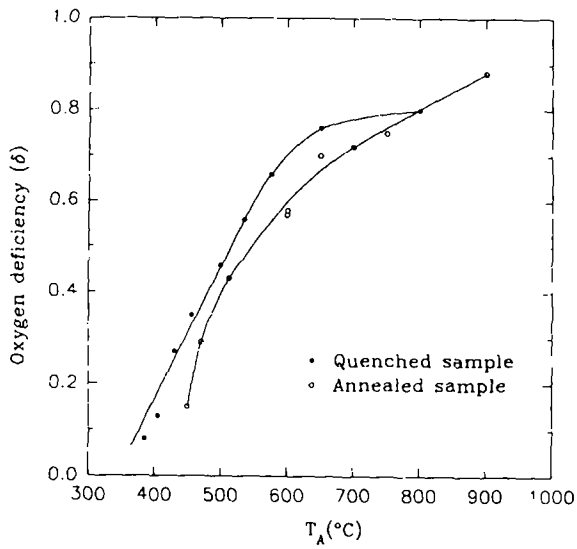

Fig. 1. Oxygen deficiency (δ) vs. annealing temperature (T_A) for annealed and quenched $(Y_{0.8}Ca_{0.2})Ba_2Cu_3O_{6.85-\delta}$ samples. The lines are a guide to the eyes.

A four-probe method was used to measure the T-dependence of the resistivity. Electrical contacts were made with pressed indium. To measure the Hall effect a five-probe arrangement was used on regularly shaped samples. The Hall voltage was obtained with a measuring current of 100 mA and a sweeping magnetic field from +8 T to −8 T. The T-range was generally between 80 and 300 K. We have also checked the magnetic-field dependence of the Hall effect for some samples. R_H was found to be linear in our T-range up to the maximum field of 8 T, with no indication of saturation in R_H as would be expected from magnetic skew scattering. Due to the metastable nature of the quenched samples, all measurements were carried out immediately after each sample processing.

3. Results and discussion

Figure 2 shows the T-dependence of the resistivity for a few representative samples. The general trend is rather similar for both the annealed and quenched samples. At high T, the resistivity is linear in T, typical of high-T_c samples. The depletion of oxygen re-

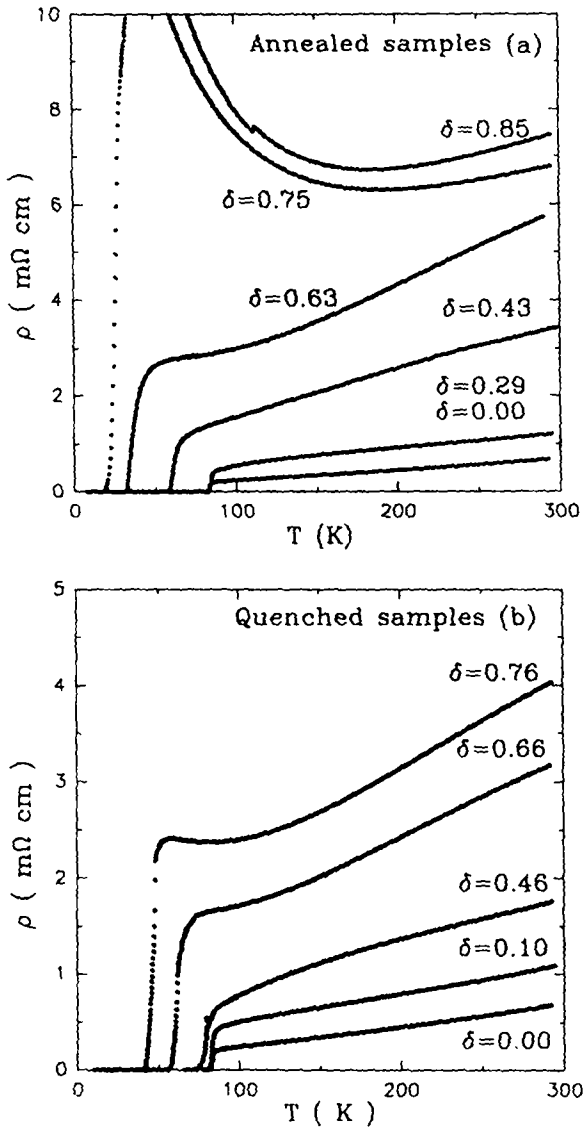

Fig. 2. Temperature (T) dependence of the resistivity (ρ) for: (a) annealed samples, and (b) quenched $(Y_{0.8}Ca_{0.2})Ba_2Cu_3O_{6.85-\delta}$ samples.

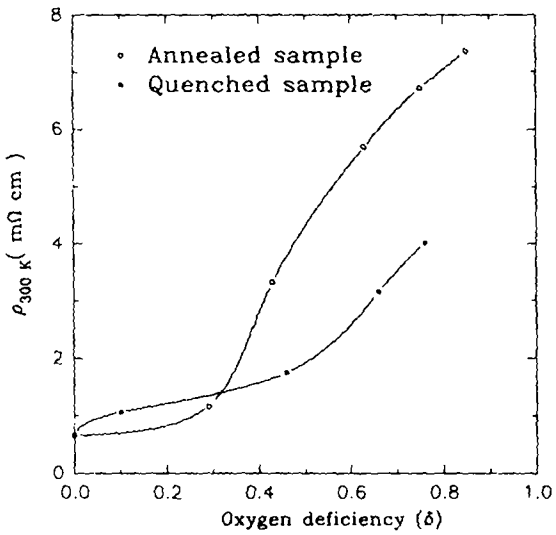

Fig. 3. Resistivity $\rho_{300\ K}$ at $T=300$ K vs. oxygen deficiency δ for annealed and quenched samples. The lines are a guide to the eyes.

sults in a large increase in resistivity, and a reduction in carrier concentration. The residual resistivity of the fully-oxygenated Ca-doped YBCO ($\delta=0$) is about zero, indicating that the sample is of high quality. In general, at the same oxygen stoichiometry, quenched samples have smaller resistivities than annealed samples. Figure 3 presents the resistivity at $T=300$ K as a function of δ for the annealed and quenched samples. Within $0<\delta<0.3$, the resistivities for both series are comparable. As will be shown later, this is the region in which T_c remains primarily constant. Beyond $\delta=0.3$, quenched samples, more disordered in nature, have substantially *lower* resistivities. The only probable explanation is that the carrier concentration in quenched samples is higher than that in annealed samples. This is further supported by the superconducting properties.

Figure 4 shows T_c versus δ, where T_c was obtained from the midpoint of the resistive transition. For comparison, the results of T_c for the oxygen deficient $YBa_2Cu_3O_{7-\delta}$ are also included [1]. A few interesting observations can be made in fig. 4. First of all, the initial T_c plateau between $0<\delta<0.15$ in pure YBCO has been substantially extended to $0<\delta<0.30$. It is known that over-doping in optimal YBCO ($T_c=92$ K) lowers T_c [2–4,10], similar to effects observed in over-doped $La_{2-x}Sr_xCuO_4$ ($x>0.15$) [13] and $Tl_2Ba_2CuO_{6+\delta}$ ($\delta>0$) [14] systems. At $\delta=0$, as shown in fig. 4, 20% Ca-doped YBCO brings T_c down to about 83 K, consistent with the available literature [7,11]. Is this caused by over-doping [10] or disorder [11]? It is known that excess carriers due to Ca are somehow compensated by the concurrent reduction in oxygen content [8,11]. We feel that this

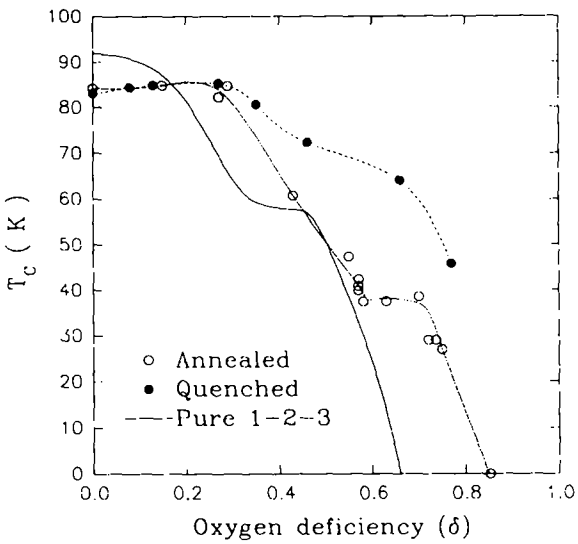

Fig. 4. T_c vs. oxygen deficiency (δ) for the $(Y_{0.8}Ca_{0.2})Ba_2Cu_3O_{6.85-\delta}$ system. The data represent midpoints of the resistive transition. The solid curve obtained from ref. [1] is for the pure $YBa_2Cu_3O_{7-\delta}$ system. The dashed lines are a guide to the eyes.

compensation is not complete for two reasons. First, as δ is increased, T_c goes up by about 2 K, an indication of over-doping in the original sample. Secondly, as shown in fig. 4, there is a shift of the T_c versus δ curve towards the high δ side in Ca-doped samples. We also believe that the effect of disorder in reducing T_c should not be ignored [11]. This is because of the fact that the reduced T_c of 83 K cannot be restored to the optimal T_c of 92 K.

Another interesting and anomalous feature in fig. 4 is that the values of T_c of quenched samples are much *higher* than those of annealed samples beyond the first T_c plateau. This is in sharp contrast to pure $YBa_2Cu_3O_{7-\delta}$, where quenched samples always have lower T_c's than annealed samples [15]. Model calculations [16,17] for YBCO have shown that the Cu–O chains, as a charge reservoir, retain more carriers when the oxygen-vacancy order is low; for example, in a quenched sample. This in turn leads to a lower carrier concentration in the $Cu–O_2$ planes, and hence a lower T_c. Veal et al. [18] have observed that T_c of a quenched sample could rise by as much as 15 K when aged at room temperature for several days. Such an increase in T_c was not caused by an oxygen intake which is not energetically viable at room temperature, but rather due to a slight enhancement in the oxygen-vacancy ordering. In Ca-doped YBCO, it seems from fig. 4 that a better ordered Cu–O chain structure, as in an annealed sample, removes more carriers from the $Cu–O_2$ plane than in a quenched sample. We also recall that the resistivity of an annealed sample is higher than that of a quenched sample as shown in fig. 3. These results suggest that Ca-doping has a strong influence on the charge storage capability of the charge reservoir. They pose a challenge to various models which rely on oxygen-vacancy order to explain the T_c versus δ curve in pure YBCO (both annealed and quenched) [16,17].

Other than the first extended T_c plateau near $\delta=0$, there also exists a second T_c plateau in the Ca-doped system particularly for the annealed system (see fig. 4). However, this plateau is lower than that in the pure YBCO by about 20 K, whereas the first plateau is only about 9 K lower. This is likely a result of the enhanced disorder effect because of the reduced screening from the free carriers. The disappearance of T_c occurs in Ca-doped samples at a higher δ than in pure YBCO samples. This is further evidence that Ca-doping supplies excess carriers beyond compensation due to the induced oxygen vacancies.

As mentioned above, the quenched Ca-doped system is most interesting in that it differs substantially from the quenched pure YBCO system. We decided to study the quenched system in more detail by measuring the Hall effect. Figure 5 presents the Hall number, n_H ($=1/eR_H$), as a function of T for a few samples. In a single-band Fermi liquid system, n_H would be the carrier concentration. But as shown in fig. 5, n_H is highly T-dependent, particularly near the optimal doping range. It becomes less so in oxygen deficient samples. Such a behavior is prevalent in many other high-T_c oxides [19]. It is difficult to reconcile the anomalous Hall effect with a conventional explanation. On the other hand, all high-T_c oxides are highly correlated systems, which should be an essential ingredient in the theory of Hall effect. Anderson [20] has proposed such a theory in the framework of the Luttinger liquid, in an attempt to account for the T-dependence of the Hall effect. The predicted T^2-dependence of the Hall angle has been observed in many high-T_c oxides [21,22]. Due to its T-dependence and the complex band structure, n_H may not represent the actual carrier concentration.

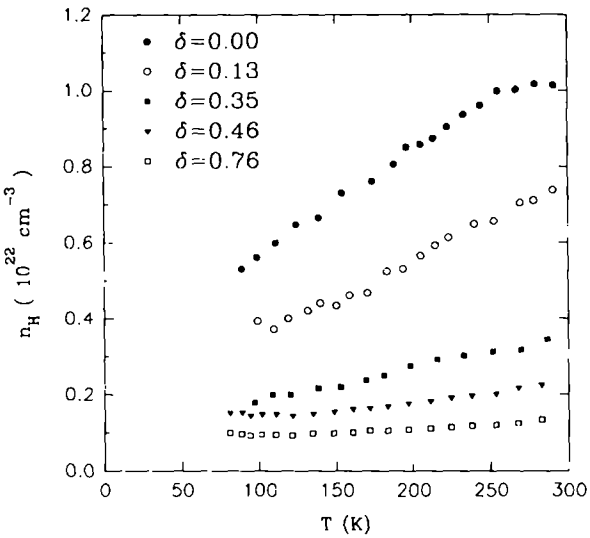

Fig. 5. T-dependence of the Hall number (n_H) for representative quenched $(Y_{0.8}Ca_{0.2})Ba_2Cu_3O_{6.85-\delta}$ samples with different oxygen deficiency.

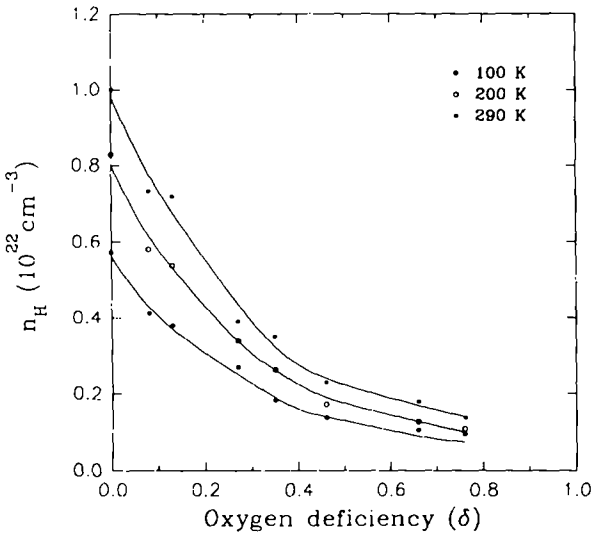

Fig. 6. Hall number (n_H) vs. oxygen deficiency (δ) for quenched $(Y_{0.8}Ca_{0.2})Ba_2Cu_3O_{6.85-\delta}$ samples. The lines are a guide to the eyes.

However, the value of n_H at a particular T correlates rather consistently with the carrier concentration determined by other methods [4,23]. In a pressure-dependence study of the Hall effect [23], it was shown that high pressure does not change the T- dependence of n_H, but simply increases n_H by a constant proportional to the pressure. This is evidence that n_H scales with the actual carrier concentration.

In fig. 6, we show the value of n_H obtained at 100, 200 and 290 K as a function of δ. n_H decreases with oxygen deficiency in a smooth fashion, despite the fact that an extended T_c plateau exists in $0<\delta<0.3$. Near $\delta=0$, n_H is lowered at a much faster rate with δ than at higher δ. This can be understood as follows. n_H is a measure of the mobile carrier concentration. Near $\delta=0$, a reduction in oxygen content reduces the mobile carrier concentration more effectively. As δ is increased, the number of localized holes also starts to be reduced, which slows down the reduction of the mobile carrier concentration.

The variation of the carrier concentration is also expected to affect the resistivity ρ. In the simple Drude model, one expects $\rho=m^*/ne^2\tau$, where m^* is the effective electron mass, and $1/\tau$ is the electron scattering rate. In fig. 7, we present the correlation between ρ and $1/n_H$ at three temperatures (100, 200 and 290 K). In every case, the $\rho \propto 1/n_H$ relation is well confirmed. This is, in fact, quite surprising, because it implies that the ratio of m^*/τ ($\propto$ slope) remains constant at a fixed T for samples with a broad variation in oxygen content. The parameter m^*/τ is

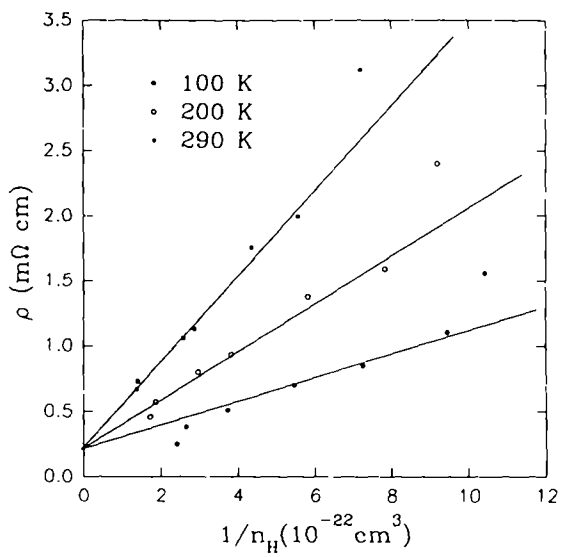

Fig. 7. Resistivity (ρ) vs. reciprocal of Hall number ($1/n_H$) at 100, 200, and 300 K for quenched samples. The straight lines are least-square fits to the data.

a Fermi surface property and is, in general, sensitive to doping. The insensitivity seen in fig. 7, if confirmed in other systems, should serve as a test for models of electron transport. Finally, let us focus on the dependence of T_c on the Hall number, which is shown in fig. 8. The T_c versus n_H curve is highly unusual compared with other high-T_c systems. Based on data of more than half a dozen systems, Whangbo and Torardi [24] suggested that T_c is an inverted parabolic function of carrier concentration in both the under-doped and the over-doped regions, i.e.

$$T_c = T_{c,max}[1 - \eta(n - n_{opt})^2] , \quad (1)$$

where $T_{c,max}$ is the maximum T_c at the optimal doping level n_{opt}. Fitting relation (1) to our data is only marginally possible for samples with low carrier concentration (under-doped). The solid line in fig. 8 represents relation (1). Clearly the over-doped region (dashed line) cannot be described by relation (1). What is most surprising is that in the over-doped region, T_c remains primarily constant even though the carrier concentration is increased by as much as 100%. Based on the data presented, we feel that the majority of the carriers supplied by 20% Ca-doping do not enter into the Cu–O_2 planes, but rather into the Cu–O chains. The initial oxygen reduction removes those Ca carriers. This process does not affect T_c, thereby creating a T_c plateau. The Ca carriers, however, do affect the resistivity and the Hall effect as shown in figs. 2 and 4. Furthermore, Ca-doping substantially alters the charge storage capability of the Cu–O chain charge reservoir.

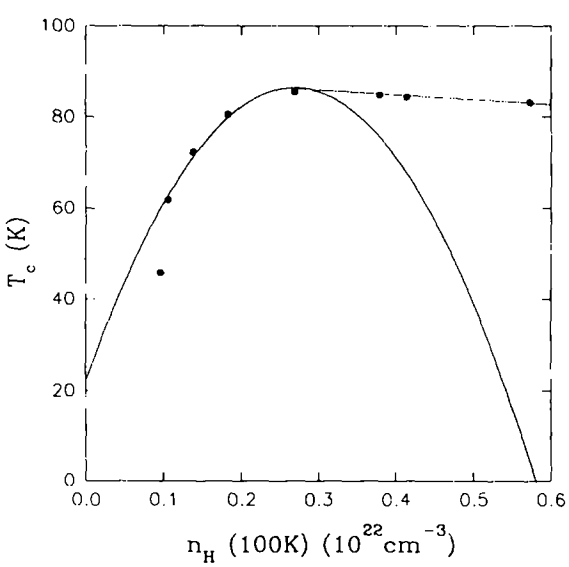

Fig. 8. Correlation between T_c and Hall number (n_H) at $T = 100$ K for quenched $(Y_{0.8}Ca_{0.2})Ba_2Cu_3O_{6.85-\delta}$ samples. The parabolic line is from relation (1) in the text.

4. Summary and conclusions

We have measured the resistivity, the Hall effect, and T_c of the $(Y_{0.8}Ca_{0.2})Ba_2Cu_3O_{6.85-\delta}$ system with varying oxygen content. In the fully-oxygenated sample, T_c is reduced to 83 K from 92 K in pure YBCO. The majority of the carriers brought about by Ca-doping, most probably, are absorbed into the Cu–O chain charge reservoir. The first T_c plateau becomes substantially extended ($0 < \delta < 0.3$), which, we believe, is caused by these excess carriers. One anomalous effect due to Ca-doping is that T_c of a quenched sample is much higher than that of an annealed sample with the same oxygen content (beyond the first T_c plateau). We also found that the resistivity of oxygen deficient samples scales linearly with $1/n_H$, the inverse of the Hall number. This means that the parameter m^*/τ remains basically constant as the oxygen content is varied. The parabolic correlation between T_c and the carrier concentration, an empirical relation true in many high-T_c systems, fails completely in the over-doped region and is marginally valid in the under-doped region. This supports our conjecture that the over-doped carriers by Ca do not go into Cu–O_2 planes. These excess carriers, though having little effect on T_c, have a strong influence on the resistivity and the Hall effect.

Acknowledgements

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