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Superconducting properties of the Mercury and Cu/C Phases

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In $HgBa_2Ca_{n-1}Cu_nO_{8+\delta}$, T_c reaches 135K for n=3 in $HgBa_2Ca_{n-1}Cu_nO_{8+\delta}$. T_c goes through a maximum versus the oxygen content for n=1,2,3 and increases with pressure for 1<n<5. The critical current densities, irreversibility line and anisotropy compare favorably with other (Bi, Tl,...) compounds. Many substitutions have been tried, which, however, did not allow to reach T_c's larger than 140K, up to now. In the $C_yCu_{1-y}Ba_2Ca_{n-1}Cu_nO_x$ cuprates, the n=3 phase has a T_c of 120K after annealing in Ar, the as prepared n=4 phase is very stable with an optimal T_c of 117K and a phase with $T_c \approx 126.5K$ (the highest T_c without toxic element) has been observed. Most of the obtained phases have also been studied under pressure.

1- The mercury family

$HgBa_2CuO_{4+\delta}$, the first member of the series has T_c=97K [1]. Therefore, record high T_c's have been obtained with n=2 (T_c = 127K) and n=3 (T_c =135K) in the optimally doped elements $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ [2, 3]. Then, T_c decreases for n larger than 3, which corresponds to underdoped elements (T_c reaches 114K, 100K and 88K respectively for n=5, n=6, n=7) [4-8]. Values of n up to 9 have been observed in some grains, by electron microscopy.

The properties of HTSC cuprates are strongly anisotropic since their conduction is much better along the CuO_2 planes in the normal state. The superconducting properties, too, are anisotropic and it is very important to measure this anisotropy, the critical current densities (in various directions), and the irreversibility line, to appreciate the interest of a new phase for applications when compared with the superconductors. The irreversibility line of 3, taken where the magnetization M(H) becomes reversible, is above that of YBCO for T>70 K, and well above those of the Bi and Tl compounds.

The anisotropy, γ, of the high T_c superconductors is inherent to the bidimensional character of their structure. It influences the normal state (resistivity: $\gamma=\rho_c/\rho_{a,b}$..), the superconducting parameters ($\xi_{a,b}/\xi_c$, $\lambda_c/\lambda_{a,b}$..) and the properties associated with the pinning of the vortex: critical current density, J_c, irreversibility line Hirr (T). It can be obtained from the resistivity in the normal state, the magnetoresistance, the reversible magnetization, torque measurements, etc... Some general trends are observed: γ increases with the number, m=1 or 2, of layers of the rock-salt block, and tends to decrease with the number, n, of CuO_2 layers. The anisotropy is small in the case of $YBa_2Cu_3O_7$ with γ=4-6, larger in Tl-1212 (g=50) and much larger in Bi-22(n-1)n and Tl-22(n-1)n, with γ values of the order of 100. It is quite remarquable that for Hg-1223 it is rather small with a value between 16 [9] and 50 [10]. Larger values are obtained for Hg-1234 or Hg-1245, but these phases are not so pure. This is in agreement with the relatively large values of $H_{irr}(T)$ for Hg-1223, which, with a high T_c and large critical current densities, must be a good candidate for the applications. This has been confirmed by magnetic measurements, which show the same general features as in most HTSC crystals: the fishtail effect, and a strong dependence of J_c versus the annealing conditions [11]. Like in other materials (YBCO, Bi, Tl families) the critical current density must improve very much in the Hg family with the quality of the crystals and the presence of columnar defects.

2-The Copper-Carbonate family

One of the most successful substitutions was obtained by replacing mercury by (Cu,C). This new copper family (of general formula $Cu_{1-x}C_xBa_2Ca_{n-1}Cu_nO_y$) needs to be prepared under pressure (70kbar) [12-15]. In the copper family, n is found to vary only from n=3 to n=6 (observed by electron microscopy).

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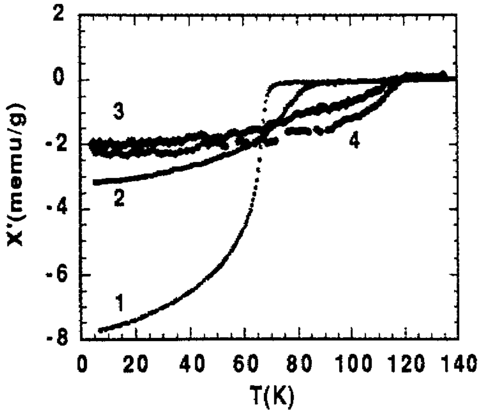

Figure 1: Effect of successive annealings at 400°C in Ar atmosphere (1: as prepared, 2: 2h, 3: 4h, 4: 4.5h) increases the T_c of (Cu,C)-1223.

In the as-prepared samples, T_c is equal to 70K for n=3 and 117K for n=4, it decreases for larger n. However, for n=3, T_c increases up to 120K after heat treatment in Ar (see fig.1).

Besides the usual transition at 117.6K corresponding to the n=4 member, we also observed a well defined transition at ≈ 126.5K, but we could not identify the material responsible for this high T_c.

We have followed the pressure dependence of T_c for the three different phases. It is easy to determine three different transition temperatures (T_{c1}, T_{c2}, T_{c3}) that correspond to different superconducting phases. $T_{c2} \approx 117$K corresponds to n= 4 [12,13] and has a small pressure dependence, going through a maximum around 10GPa. Since dT_c/dP is small in optimally doped samples, we can infer that the n=4 member of the family is nearly optimised under the present synthesis conditions (13-14).

The most interesting result is the marked increase of the highest T_c, namely $T_{c3} \approx 126.5$K, observed in samples of this system. At the highest pressure used, 21GPa, T_{c3} **attains ≈136K**. It might still increase if higher pressures were applied.

This is the second highest T_c ever observed for a superconducting sample under pressure, the first being that of the n=3 member (Hg-1223) of the mercury based HTSC cuprates.

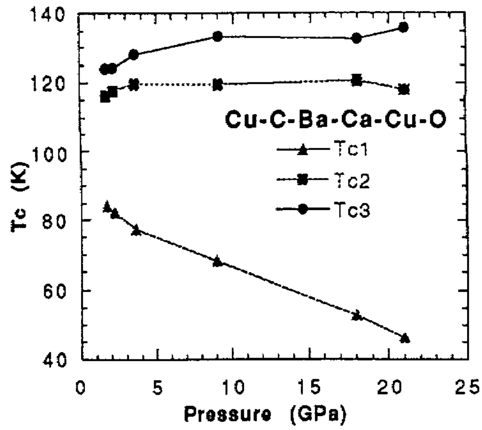

Figure 2: Pressure effect for various (CuC) phases.

In summary, the discovery of new HTSC phases, which already show excellent capacities for applications, is quite promising, even though T_c has not yet reached values of 160K observed under pressure (in Hg-1223). The efforts towards the applications are also fruitfull, and there is no doubt that these materials will have an increasing importance in the future.

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