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NEW high temperature superconducting MATERIALS

J. L. THOLENCE, O. LABORDE, A. SULPICE, L. PUECH, C. ACHA,
M. NUNEZ-REGUEIRO, J. J. CAPPONI[1], C. CHAILLOUT[1], M. ALARIO-FRANCO[1],
M. MAREZIO[1], P. BORDET[1], S. M. LOUREIRO[1], S. N. PUTILIN[1,2],
and E. V. ANTIPOV[1,2]

Centre de Recherches sur les Très Basses Températures,
and [1] Laboratoire de Cristallographie, Laboratoires associés à l'Université Joseph Fourier,
C.N.R.S., BP 166, 38042 Grenoble-Cédex, France
[2] Department of Chemistry, Moscow State Univ., Moscow 119899, Russia

The synthesis and superconducting properties of new HTSC phases are presented. In Hg-cuprates high critical temperatures T_c are reached with a maximum value of 135 K for $n = 3$ (n = number of CuO_2 planes) in $HgBa_2Ca_{n-1}Cu_nO_{8+d}$. T_c goes through a maximum as a function of the oxygen content and increases with pressure for $1 < n < 5$. It can reach 160 K under 350 kbars in Hg-1223. However, up to now, such high critical temperatures have not been reached at atmospheric pressure by chemical substitutions. For the pure Hg-1223 phase, the critical current densities, irreversibility line and anisotropy compare favorably with other (Bi, Tl, $\cdots$) compounds. Phases with two mercury planes have been synthesized, but their T_c remain smaller than for one mercury plane. In the (Cu,C)-cuprates, prepared under pressure, a T_c of 117 K is obtained for $n = 4$, and for $n = 3$, an oxygen reduction changes T_c from 80 K to 120 K. Finally, a minority phase with T_c up to 129 K (increasing with pressure) has been observed but not identified.

KEYWORDS: Hg-cuprates, pressure effect, critical current densities, irreversibility line, synthesis of new high T_c superconductors

§1 The Mercury family

Since the discovery of superconductivity at high temperature in copper mixed oxides by Bednorz and Muller (1986) a number of new compounds and of families of compounds has been discovered. Besides $YBa_2Cu_3O_7$ with a T_c of 94K, the highest T_c have been obtained for n=3 in the Bi and Tl families of general formulas: $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+2+d}$ and $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+2+d}$ with respectively T_c =108K for Bi-2223 and T_c =125K for Tl-2223. The structures of these compounds have some common features. They are made of blocks of CuO_2-Ca-CuO_2- layers having the perovskite structure which alternate with blocks made of BaO-TlO-TlO-BaO or SrO-BiO-BiO-SrO having the rock-salt structure. The perovskite blocks are at the origin of the superconductivity when the Cu valence is higher than 2 and in the range of +2.1 to +2.2. Moreover, for a given compound, T_c is strongly dependent on the valence of copper in the CuO_2 planes, which itself strongly depends on the oxygen content in the rock-salt blocks which are called charge reservoirs.

The $HgBa_2CuO_{4+d}$ compound has been obtained by substituting one Cu (of the chains) of $YBa_2Cu_3O_7$ by mercury, and reducing the number of CuO_2 planes from 2 to 1. The critical temperature, T_c =97K, of this n=1 compound was among the highest of all cuprates with one CuO_2 layer (except for $Tl_2Ba_2CuO_{6+d}$ which has a Tc of up to 100K)[1]. Therefore, record high T_c's have been obtained with n=2 (T_c = 127K) and n=3 (T_c =135K) in the mercury family $HgBa_2Ca_{n-1}Cu_nO_{2n+2+d}$ [2, 3]. Then, T_c decreases for n larger than 3, like in other known families[4] and values of n up to 9 have been observed in some grains, by electron microscopy. It is possible to prepare the samples from the precursors by a classical technique or under pressure (around 20kbar) for n=1-3, and only under pressure for n>3. This last technique, besides its safety, allows to obtain samples with a high oxygen content (overdoped). Further annealing can be made to vary the oxygen content, and to obtain the maximum of the curve of T_c versus oxygen content (or copper valence), as for instance in Hg-1212[5]. Moreover, T_c has been found to strongly depend on the applied pressure, even when the maximum T_c (versus oxygen content) has been reached for different elements of the mercury family[6-7]. In particular, values as high as 164K (onset T_c) have been mentioned for Hg-1223[7]. This increase of T_c is associated with changes in the structure. In particular a decrease of the c lattice parameter, and more precisely of the distance of the apical oxygen from the CuO_2 planes is observed[8]. Thus, it must be possible to reach such high T_c values if similar effects can be obtained by chemical pressure. Several substitutions have been tried on the Ba and Hg sites. Many of them give superconducting materials [9-10], but without improvement (except may be for a partial substitution by Tl which gives a T_c of 138K [11] or by Pb which gives a T_c of 143K[12]). Finally, compounds with two mercury layers (analogous to the Tl_2- and Bi_2- families) have been synthesized. Their superconducting properties do not appear very interesting (T_c = 70K)[13]. However, recent resistivity measurements under pressure show that they can be improved.

§2 The Copper-Carbonate family

One of the successful substitution on the mercury site has been obtained by trying to put silver instead of mercury [14-16]. In fact silver does not enter in the structure but copper is found on one Hg site over two (50% of Cu on the mercury sites) the other Hg site being occupied by carbonate $(CO_3)^{2-}$ ions. Moreover, and on the contrary of the mercury family, this copper family (of general formula $Cu_{1-x}C_xBa_2Ca_{n-1}Cu_nO_y$) needs to be prepared under pressure (70kbar). The presence of carbonates comes naturally from the carbon dioxide of the air which reacts with the starting precursor. In the copper family, n is found to vary only from n=3 to n=6 (observed by electron microscopy). In the as-prepared samples, T_c is equal to 70K for n=3 and 117K for n=4, it decreases for larger n. It would be the only case where T_c would be maximal for n=4 instead of n=3 in all the other known cuprate families (except for Tl-1223 and Tl-1234 which have the same T_c =120K).

For every synthesis performed at ≈800°C and under 8GPa besides the usual transition at 117.6K corresponding to the n=4 member, often mixed with other members of the family with lower critical temperatures, we also observed a well defined transition at ≈ 126.5K (Figure 1). This temperature is very close to the highest observed T_c within the thallium family of cuprates, and only second to the best mercury based one at atmospheric pressure (Tc=133K for the n=3 member of this family with optimal doping). The amount of superconducting phase with Tc=126.5K is very small[17]. It can be estimated to ≈1% as compared with about 60% for the n=4 member of the cupro/carbonate family observed in the same synthesis, from magnetization measurements on ceramics. It could even be much less as suggested by ac susceptibility measurements on powders. Although we could not identify the material responsible for this high T_c, one can reasonably assume that it is either an optimised member of the cupro/carbonate family, or that, under the high pressure used during the synthesis, silver has entered the structure in the Charge Reservoir Block (CRB), improving the superconducting properties. Obviously, more work is needed in order to increase the amount of this phase in the sample so as to properly identify it.

Resistivity under pressure:

Although for the reasons indicated above we have not been able as yet to prepare in pure form a single member of the cupro/carbonate family, we have been able to follow the pressure dependence of T_c for the three different phases. Selecting chips from the sample that showed Meissner expulsion below 126.5K we measured their electrical resistance as a function of temperature in the diamond anvil apparatus used previously[17]. As shown in Figure 1 it is easy to determine three different transition temperatures (T_{c1}, T_{c2}, T_{c3}) that correspond to different superconducting phases.

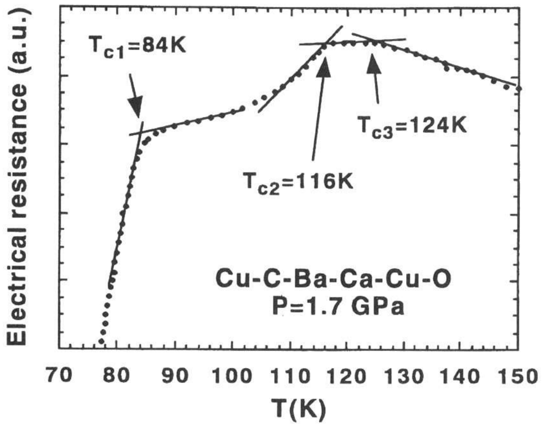

Figure 1: Existence of three different phases in a (Cu,C) compound prepared under pressure.

We attribute T_{c2} ≈ 117K to the n=4 member of the family of cupro/carbonates[14,17]. As shown in Figure 2, T_{c2} has a small pressure dependence, it goes through a maximum around 10GPa. As it is usually assumed that, due to a most subtle compromise between oxygen content and interatomic distances, 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 (see also reference 17).

T_{c1} ≈ 80K should correspond to the n=3 member of the cupro/carbonate family. It decreases strongly with pressure indicating clearly that overdoping in oxygen exists in this phase, confirming previous observations[17] (see figure 2).

The most interesting result is the marked increase of the highest T_c, namely T_{c3}≈126.5K, 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.

Undoubtedly, more work has to be done to synthesize monophase samples of these high pressure phases, to fully characterize their superconducting -and other- properties, and identify the unknown phase with the highest T_c. Yet the present results show that, in the absence of toxic thallium or mercury, very high critical temperatures can be achieved in this cupro/carbonate family.

The structural refinement based on neutron diffraction powder data reported by Shimakawa et al.[18] confirmed the structure envisaged by high resolution electron microscopy. However, it is not very conclusive about the local arrangement of the (Cu,C) CRB block, which should reveal the doping mechanism and eventually allow one to optimize the superconducting properties. Chaillout et al. [19] also collected neutron powder data on a sample containing 60% of (Cu,C)-1234, 19% of (Cu,C)-1223, and other impurities, some of which have not been identified. This refinement is not conclusive either, but together with the results of other experiments allows us to make some conjectures about the structure of the CRB.

These cupro/carbonates seem to be insensitive to heat-treatments under oxygen pressure. This would indicate that the CRB of these compounds does not contain mobile oxygen atoms as the Hg counterparts. In this case the Cu cations of the CRB would have the dumbbell coordination and the only oxygen atom of this layer would be that bonded to C. This

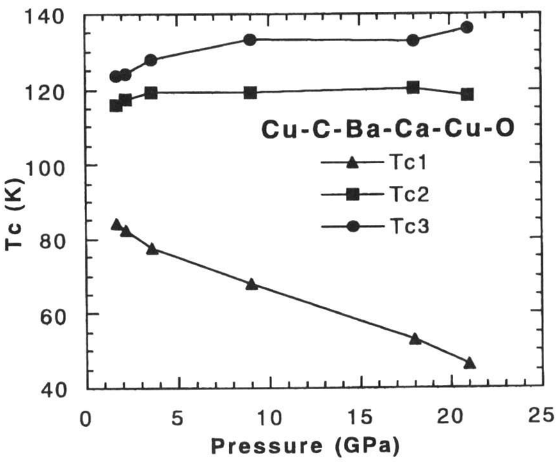

Figure 2: Effect of the pressure on Tc of various (CuC) phases.

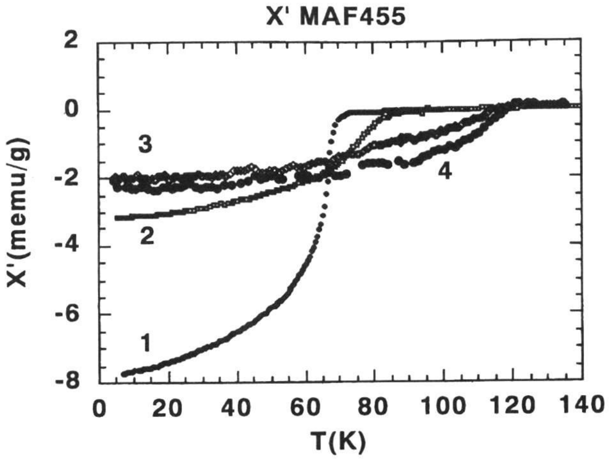

Figure 3: The effect of successsive annealings at 400°C in Ar atmosphere (1: as prepared, 2: 2h, 3: 4h, 4: 4.5h) increases the T_c of (Cu,C)-1223.

conjecture is corroborated by the results of the structural refinement of reference 17. The formula deduced from preliminary results would be $Cu_{0.22}C_{0.78}Ba_2Ca_3Cu_4O_{11}$, which corresponds to v_{Cu}=2.16 v.u. for the Cu cations of the CuO_2 layers. This value is very close to the critical Cu valence corresponding to the optimal carrier concentration for superconductivity. The same reasoning for the n=3 member yields v_{Cu}=2.22 v.u. which would correspond indeed to an overdoped state as the high pressure experiments indicate. In fact, successive annealings in Ar atmosphere result into larger T_c for (Cu,C)-1223 which tends to saturate to 120K.

As revealed by high resolution electron microscopy, some crystallites of the cupro/carbonates contain sequences corresponding to the n-5, 6, or 7 members. The existence of the higher members of the series, shared with the Hg-based cuprates, would indicate that the CuO_2 layers are flat as in the Hg counterparts. For example, to obtain the higher members of the Bi-based layered cuprates, the layer-by-layer deposition technique has to be used.

This suggests that T_c could continue to increase with n if the charge transfer to the CuO_2 planes was sufficient. Moreover, an unidentified phase (of the order of 1% in volume, as determined by susceptibility on powders) with T_c as high as 129K has often been observed in these compounds. It is the highest T_c in a compound without mercury or thallium.

Many attempts have been made to realize an **infinite layer compound**, where an infinite number of CuO_2 planes (non superconducting when they are only separated by Ca or Sr layers) would become superconducting if they were correctly charged. However, when some superconductivity is found in these materials, it appears that it is due to other phases, for instance with 2 CuO_2 layers. Moreover, the superconducting properties obtained are not excellent and well reproducible (maximum T_c = 110K and 30% superconducting volume). The deposition, layer by layer, is another way to obtain new compounds and structures which would not exist naturally, even after synthesis under pressure.

§3 Properties and Applications

The properties of HTSC cuprates are strongly anisotropic since the conduction is much better along the CuO_2 planes in the normal state. The superconducting properties, too, are anisotropic and, when a new compound is discovered, it is very important to measure its anisotropy, the critical current densities (in various directions), and the irreversibility line, to appreciate its interest for the applications as compared with existing superconductors. Some of these properties can be estimated as soon as a pure phase is synthezised in the form of ceramics. The growth of crystals or films is then needed for a detailed study.

The critical current densities and irreversibility lines of sintered compounds of the series $HgBa_2Ca_{n-1}Cu_nO_{2n+2+d}$ with n = 1-5 have been determined. They are obtained in a wide temperature range and under large magnetic field (20 tesla) from magnetoresistance or magnetization measurements. The magnetization of Hg-1223 has been measured in a magnetometer using the extraction method, where the sample is moved from one to the other of the pick-up coils. The results are presented in figure 4, where M(H) is reported for fields up to 14T and several temperatures.

From the hysteresis cycles one can deduce [20] the critical current density, J_c, either from the saturated remanent magnetization RM in null field which gives J_c (H=0) or from the difference (DM) between the magnetization values taken in the same increasing or decreasing field (H). Using the Bean model, the intragrain J_c, can be estimated from a ceramics by taking an average grain size of 10 mm, observed by electron microscopy and writing J_c (A/cm^2) = 30 000 RM or 15 000 DM (with RM and DM in cm^3). Although the absolute J_c value is not very accurate (due to the uncertainty on the grain size) the main conclusions about its field and temperature dependence remain correct.

The field dependence of J_c for different temperatures is rather strong since J_c decreases by a factor five between 0 and 14 T at 4.2 K, which is two times larger than for $YBa_2Cu_3O_7$ in the same conditions. However these performances can be improved. The temperature dependence of the zero field critical current density J_c (T) decreases

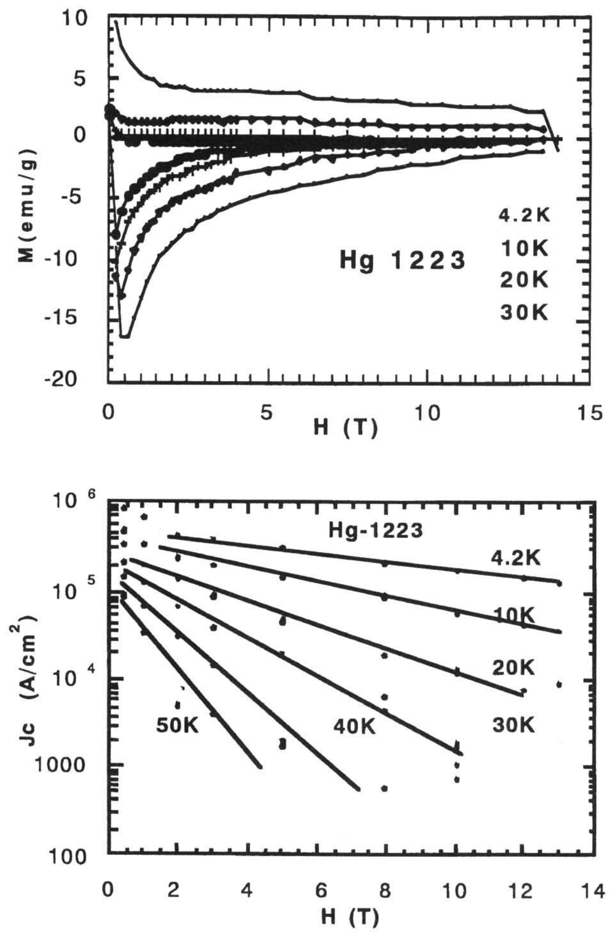

Figure 4. Magnetization versus H for a ceramic of Hg-1223 and the deduced critical current density for different temperatures.

exponentially in a large temperature range, except below 10 K where J_c increases faster when T decreases, and close to T_c where a power law is expected. The thermal dependence of $J_c = A \exp(-T/50)$ is slower than in YBCO where an exp(-T/20) variation has been observed in single crystals for two directions of the applied field. Therefore, if the field dependence of J_c is stronger in Hg-1223 than in YBCO its temperature dependence is weaker (better).

The irreversibility line $H_{irr}(T)$, can be taken at the point where the magnetization M(H) becomes reversible, and DM=0. The occurence of an irreversibility line with $H_{irr}(T)$ well below the critical line $H_{c2}(T)$ in the H(T) phase diagram, is a common feature of all the copper oxide superconductors. Above the irreversibility line there is a melting of the vortex lattice and the critical current density deduced from the magnetization is null since DM=0 (this is not true for the current which still can flow in the perovskite blocks above the irreversibility line, as shown by resistive measurements of the critical current density of films). The irreversibility line of Hg-1223 is above that of YBCO for T>70 K, and well above those of the Bi_2- and Tl_2- families.

A similar behavior is observed for the irreversibility lines obtained from magnetoresistance measurements (in this case the irreversibility lines have been taken at 1/100 of the normal state resistance) [20] and shown in figure 5.

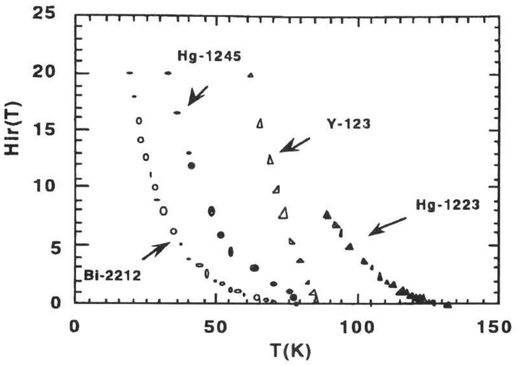

Figure 5. Irreversibility lines for some mercury and other HTSC.

Different factors are known to influence the position of the irreversibility line. First, the quality of the material and the optimisation of its superconducting properties (high T_c, large superconducting volume, small amount of large defects and impurities). Second, a large anisotropy leads to a smaller coupling of the vortices (trapped on 2D pancakes) which can move more easily resulting into a small H_{irr} (T) for a given reduced temperature T/T_c. Third, the increase of the pinning force increases, on the opposite, the $H_{irr}(T)$ line: this can be obtained by various substitutions or defects in the structure.

The anisotropy is characterized for instance by $e = (M/m)^{1/2}$, the square root of the effective masses along the c axis (M) and in the a-b plane (m) as deduced from resistivity measurements. The anisotropy is small in the case of $YBa_2Cu_3O_7$ with e = 4-6, much larger in $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+2+d}$ and $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+2+d}$, with e values of the order of 100. It is quite remarquable that for Hg-1223 it is rather small with a value of 16 (larger values are obtained for Hg-1234 or Hg-1245, but these phases are not so pure) [20].This is in agreement with the relatively large values of $H_{irr}(T)$ for Hg-1223, which, together with a high T_c, must have large critical current densities, and must be a good candidate for the applications.

As expected, the anisotropy is larger in systems where the charge reservoir blocks contain two planes (Tl_2-, Bi_2-, families) than in $YBa_2Cu_3O_7$ or the Hg- family. A strong anisotropy is found in other superconducting properties, in particular the critical current density is the highest when the current flows along the CuO_2 layers. It remains constant in large fields when the magnetic field is parallel to these planes. Therefore, for the applications it is important to realize these conditions: for instance coils made of ribbons with the CuO_2 layers in the plane of the ribbon (the highest field being then parallel to CuO_2 planes), or to use HTSC with a small anisotropy.

Another very important problem consists to make wires or ribbons from materials which naturally exist in the form of ceramics. It is then important to obtain the growth of crystals as large as possible which have good superconducting contacts with the next crystals, to make wires with large critical current densities. Obviously, it is easier to make short superconducting connections (a few cms long) as superconducting leads for superconducting coils. It is also easy to make cylinders for magnetic screening or to trap a magnetic field, as well as to realize a superconducting cavity. But the best performances will be obtained only if the number of grains is limited and the contact between grains optimized (in quality and size). The addition of Ag (a few per cent) helps to increase the size of the grains and the contact between them (not for the Hg-family!). Much work has been made to realize rods or wires of $YBa_2Cu_3O_7$ and ribbons of $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+2+d}$ and $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+2+d}$ sheathed with silver and some superconducting coils have already been made. Such coils have apparently weak performances: 5-6 T, but (since they have larger critical fields) they can be put inside classical superconducting coils (giving up to 20T) and add their field to this 20T field.

Films of all the main superconducting phases, have very good performances in terms of critical current densities. Recently, and in spite of the volatility of HgO, films of Hg-1212 have been successfully prepared[20]. Very large critical current densities have been measured (10^8 A/cm^2 at 77K in the best conditions, with J and H in the a-b plane, and J perpendicular to H) in various experimental conditions [21].

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 (or higher values). 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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