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NEW SUPERCONDUCTING OXIDES IN THE Bi-Sr-Ca-Cu-O SYSTEM: MAGNETIC MEASUREMENTS AND STRUCTURAL DETERMINATION

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Abstract. – Detailed neutron diffraction structure analysis of $Bi_2Sr_2CaCu_2O_8$ is reported. The effects of Pb-substitution on $Bi_2Sr_2CaCu_2O_8$ and $Bi_2Sr_2CuO_6$ are discussed, and magnetization measurement results on the 110 K phase in the Bi-Sr-Ca-Cu-O system are given.

Since the discovery of high T_c superconductivity in the Bi-Sr-Ca-Cu-O system [1], two superconducting phases have been unambiguously identified, namely $Bi_2Sr_2CuO_6$ ($T_c \approx 10$ K) and $Bi_2Sr_2CaCu_2O_8$ ($T_c \approx 80$ K), hereafter denoted as 2201 and 2212. The presence of transition temperatures around 110 K in mixed phase samples suggested the existence of a third phase, the composition of which could be 2223, based on an analogy with the later discovered thallium compounds [2]. We report here a detailed structural analysis of the 2212 phase and physical characterizations of the 110 K phase.

Three alternative models for the structure of $Bi_2Sr_2CaCu_2O_8$ were first proposed on the basis of X-ray single crystal diffraction data [3]. Then, Bordet *et al.* [4] used powder neutron diffraction to show that the double Bi-O layers do not adopt the usual Aurivilius structure, but are arranged in an NaCl-type structure. The problem with this model, refined in the Fmmm space group, is that the in-plane Bi-O distances are too long to satisfy the normal Bi^{3+} coordination. In fact, these oxygens appear disordered in this model. We show here a more precise analysis of our neutron data allowing a better determination of the Bi co-ordination.

As the space group Amaa or its non-centric subgroup A2aa have been confirmed by convergent beam electron diffraction [5], the neutron data were refined in Amaa by permitting all atoms to move off the y-axis special position of the Bordet *et al.* structure taken as the starting model. Only the BiO plane oxygen O3 (which appeared "disordered" in Fmmm) was much displaced. In Amaa, the best refinement was obtained by splitting O3 between two sites either side of the center of the Bi-square. In an attempt to remove the need for split atoms, we simply removed the center of symmetry (space group A2aa). O3 was then not constrained in any way, and immediately moved to occupy a position close to a pair of Bi atoms. As these refinements were carried out in the subcell, they cannot take into account the displacements of the Bi atoms related to the existence of the ≈ 4.7 Å superstructure along the a-axis.

In the resulting structure (see Tab. I), each Bi has three close oxygen neighbours at between 2.12 Å and 2.28 Å, opposite to the Bi^{3+} "lone pair". This co-ordination is more satisfactory than that obtained with Fmmm, and all Bi remains essentially Bi^{3+}, as there is no experimental evidence for Bi^{5+}. The formula is close to $Bi_2Sr_2CaCu_2O_8$

The substitution of Bi by Pb in the 2201 and 2212 phases as also been studied. It was found in both cases that as much as 0.4 Pb per unit formula can be incorporated without detection of extra phases by X-ray powder diffraction. Preliminary a.c. susceptibility measurements on powder and single crystal samples of both phases have been performed. They seem

Table I. – *Atom positions, thermal and occupancy factors,* Bi-O *and* Cu-O *distances* (Å) *for* $Bi_2Sr_2CaCu_2O_8$.

Atom	x	y	z	B	n
Bi 8d	0	0.239(3)	0.4454(2)	4.5(2)	7.5(2)
Ca 4c	0	1/4	1/4	1.8(3)	3.9(2)
Sr 8d	0	0.737(2)	0.3586(2)	2.9(2)	8.3(2)
Cu 8d	0	0.264(2)	0.3041(2)	2.0(1)	8.7(2)
O11 8d	1/4	−0.011(4)	0.3109(2)	0.5(1)	8
O12 8d	1/4	0.496(5)	0.2905(2)	0.5	8
O2 8d	0	0.269(5)	0.3772(5)	5.4(4)	7.4(2)
O3 8d	0.378(6)	0.359(6)	0.4397(6)	9.6(9)	8.6(2)

Bi	−O2	2.12(2)	Cu	−O11	2.03(2), 1.94(2)
Bi	−O3	2.15(3)	Cu	−O12	1.90(2), 1.92(2)
Bi	−O3	2.28(2)	Cu	−O2	2.26(2)

$a = 5.4095(4)$Å, $b = 5.4202(4)$Å, $c = 30.9297(25)$Å

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to indicate an increase of T_c for the Pb-substituted 2201 phase, and a ≈ 100 K transition for the Pb-substituted 2212 samples (Fig. 1). X-ray precession photographs and electron diffraction studies reveal the presence of superstructures for both phases which are different from those observed with the corresponding unsubstituted compounds.

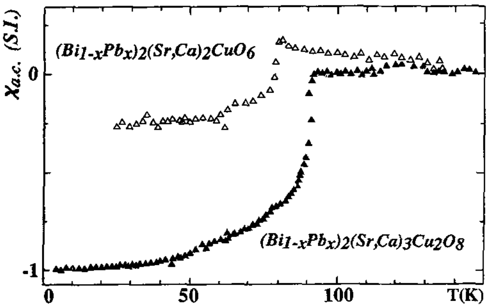

Fig. 1. – A.c. susceptibility curves for Pb substituted 2212 and 2201 polycristalline samples.

It is now confirmed that a series of superconducting compounds of formula $Bi_2Sr_2Ca_{n-1}Cu_nO_{4+2n}$ exits with $n = 1, 2, 3$. A crystal of the $n = 3$ phase has been observed to be superconducting at 103 K [2]. This result confirms other analyses which have shown the presence of a minor phase of this composition in superconducting samples *containing simultaneously* the major phase 2212 with a T_c of 85 K and a small fraction of the sample having a transition around 110 K [6].

We have prepared samples starting from different compositions of Bi_2O_3, $SrCO_3$, $CaCO_3$ and CuO at different firing temperatures and annealing times. The largest fraction of the superconducting phase having a T_c of 110 K that we have obtained reaches 15 % of the sample volume. The powders of initial composition $Bi_2Sr_{1.5}Ca_{1.5}Cu_2O_8$ were fired at 800 °C for 12 hours in air and after grinding, a second firing of 12 hours at 865 °C in oxygen was applied to the pressed pellets. A fraction of about 1 % of superconducting phase at 110 K was obtained. By annealing in oxygen at 880 °C for 48 hours, this fraction has increased up to 15 %.

The Meissner and the screening effects are always identical between 90 K and 110 K as observed in figure 2 in all our samples. This property shows that the superconductivity observed below 110 K takes place in a well-crystallized phase, in agreement with other findings. No enhancement of H_{c_1} is observed. Then, this superconductivity is established in crystallites having dimensions larger than the London penetration depth. The reversibility of the magnetization *versus* field and temperature gives us the opportunity of studying the thermodynamical properties of this phase. The condensation energy is given by the area under the magnetization curve:

$$\int_0^{H_{c_2}} (M_s - M_n)\,\mathrm{d}H = -H_c^2/8\pi.$$

A minimum value for this area can be extrapolated in high fields at different temperatures. The volume fraction of the sample having $T < T_c < T + \mathrm{d}T$ is assumed to be $\mathrm{d}T/T_{c_0}$ with T_{c_0}=110 K. This distribution leads to a linear decrease of the superconducting volume with temperature as observed in figure 2. If the thermodynamical critical field is assumed to vary as $H_c = H_0\left(1-(T/T_c)^2\right)$, there is a simple relation between the specific heat coefficient γ, T_c and H_0 : $H_0^2 = 2\pi\gamma T_c^2$. Assuming that the particles of the distribution have the same γ but different T_c's, we can calculate using this distribution the mean square of H_c:

$$H_c^2 = 2\gamma/T_{c_0}(T_{c_0}^3/3 - 2T^2T_{c_0} - T^4/T_{c_0}^4 + 8/3T^3/T_{c_0}^3).$$

We have determined *a minimum of* H_c^2 at different temperatures, and deduced a minimum γ value of about 10 mJ/mole.K^2 using the magnetization curves obtained at 100, 95 and 90 K. Such a γ value is similar to that already evaluated for the 2212 phase from specific heat measurements around 85 K [7].

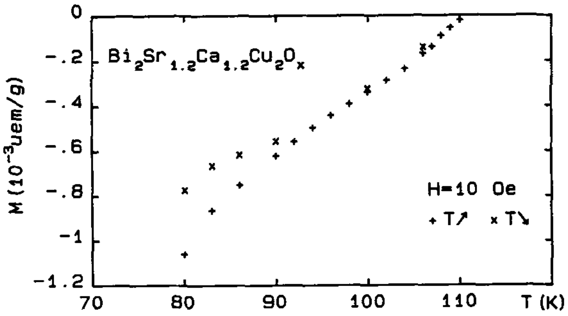

Fig. 2. – The zero-field cooled susceptibility (+) and the field-cooled susceptibility (×) in 10 Oe plotted *versus* temperature. The increase of the superconducting volume below 85 K is due to the "2212" phase. The total susceptibility of this powder sample corresponds to ≈ 70 % of superconducting volume at 4 K.

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