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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 Bi₂Sr₂CaCu₂O₈ is reported. The effects of Pb-substitution on Bi₂Sr₂Ca₃Cu₄O₁₀ and Bi₂Sr₂Ca₃Cu₄O₁₀ 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 Tc superconductivity in the Bi-Sr-Ca-Cu-O system [1], two superconducting phases have been unambiguously identified, namely Bi₂Sr₂CaCu₂O₈ (Tc ≈ 10 K) and Bi₂Sr₂Ca₃Cu₄O₁₀ (Tc ≈ 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 Bi₂Sr₂Ca₃Cu₄O₁₀ 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 Aurivillius structure, but are arranged in a 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 Bi³⁺ 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 Amma or its non-centric subgroup A2aa have been confirmed by convergent beam electron diffraction [5], the neutron data were refined in Amma 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 Amma, 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 Bi³⁺ “lone pair”. This coordination is more satisfactory than that obtained with Fmmm, and all Bi remains essentially Bi³⁺, as there is no experimental evidence for Bi⁵⁺. The formula is close to Bi₂Sr₂Ca₃Cu₂O₈.

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 Bi₂Sr₂Ca₃Cu₂O₈

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>B</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi</td>
<td>0</td>
<td>0.239(3)</td>
<td>0.4454(2)</td>
<td>4.5(2)</td>
<td>7.5(2)</td>
</tr>
<tr>
<td>Ca</td>
<td>1/4</td>
<td>1/4</td>
<td>1.8(3)</td>
<td>3.5(2)</td>
<td></td>
</tr>
<tr>
<td>Sr</td>
<td>0</td>
<td>0.377(2)</td>
<td>0.3586(2)</td>
<td>2.9(2)</td>
<td>8.3(2)</td>
</tr>
<tr>
<td>Cu</td>
<td>0</td>
<td>0.364(2)</td>
<td>0.3041(2)</td>
<td>2.0(1)</td>
<td>8.7(2)</td>
</tr>
<tr>
<td>O₁₁</td>
<td>1/4</td>
<td>-0.011(4)</td>
<td>0.3109(2)</td>
<td>0.5(1)</td>
<td>8</td>
</tr>
<tr>
<td>O₁₂</td>
<td>1/4</td>
<td>0.496(5)</td>
<td>0.2905(2)</td>
<td>0.5</td>
<td>8</td>
</tr>
<tr>
<td>O₂</td>
<td>0</td>
<td>0.269(5)</td>
<td>0.3772(5)</td>
<td>5.4(4)</td>
<td>7.4(2)</td>
</tr>
<tr>
<td>O₃</td>
<td>0.378(6)</td>
<td>0.359(6)</td>
<td>0.4397(6)</td>
<td>9.6(9)</td>
<td>8.9(2)</td>
</tr>
<tr>
<td>Bi</td>
<td>-0.22(2)</td>
<td>0.03(2)</td>
<td>0.03(2)</td>
<td>0.9(2)</td>
<td></td>
</tr>
<tr>
<td>Bi</td>
<td>-0.22(2)</td>
<td>0.03(2)</td>
<td>0.03(2)</td>
<td>0.9(2)</td>
<td></td>
</tr>
<tr>
<td>Bi</td>
<td>-0.22(2)</td>
<td>0.03(2)</td>
<td>0.03(2)</td>
<td>0.9(2)</td>
<td></td>
</tr>
</tbody>
</table>

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to indicate an increase of $T_c$ for the Pb-substituted 2201 phase, and a $\approx 100$ 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.

It is now confirmed that a series of superconducting compounds of formula $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{4+2n}$ exists 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 $\text{Bi}_2\text{O}_3$, $\text{SrCO}_3$, $\text{CaCO}_3$ and $\text{CuO}$ 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 $\text{Bi}_2\text{Sr}_{1.5}\text{Ca}_{1.5}\text{Cu}_2\text{O}_8$ 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. 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 $\gamma$, $T_c$ and $H_0$: $H_c^2=2\gamma/T_c$. Assuming that the particles of the distribution have the same $\gamma$ but different $T_c$'s, we can calculate using this distribution the mean square of $H_c$:

$$H_c^2=2\gamma/T_c(2T_c^3/3-2T^2T_c-2T_c^4/T_c+8/3T^3/T_c^3).$$

We have determined a minimum of $H_c^2$ at different temperatures, and deduced a minimum $\gamma$ value of about 10 mJ/mole.K² using the magnetization curves obtained at 100, 95 and 90 K. Such a $\gamma$ value is similar to that already evaluated for the 2212 phase from specific heat measurements around 85 K [7].

$$\int_0^{H_c} (M_s-M_n) dH = -H_c^2/8\pi.$$