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Superconductivity up to 110 K in $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ compounds

P. Lejay ⁽¹⁾, P. de Rango ⁽¹⁾, A. Sulpice ⁽¹⁾, B. Giordanengo ⁽¹⁾, R. Tournier ⁽¹⁾, R. Retoux ⁽²⁾, S. Deslandes ⁽²⁾, C. Michel ⁽²⁾, M. Hervieu ⁽²⁾ and B. Raveau ⁽²⁾

⁽¹⁾ Centre de Recherches sur les Très Basses Températures, C.N.R.S., BP 166X, 38042 Grenoble Cedex, France

⁽²⁾ Laboratoire de Cristallographie et de Chimie du Solide, ISMRA, Université de Caen, 14032 Caen, France

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Résumé. — Nous avons étudié dans le système Bi-Sr-Ca-Cu-O le composé responsable de la supraconductivité jusqu'à 110 K, de formule idéale $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$. Les mesures d'aimantation montrent la présence de deux phases dans les échantillons, avec des transitions à 80 K et 110 K. En faisant varier la composition et les traitements thermiques de ces échantillons, nous avons réussi à augmenter la proportion de la phase supraconductrice jusqu'à 110 K. L'effet Meissner atteint 30 % de $-3/8 \pi$ à 90 K pour les échantillons non dopés et 50 % pour ceux dopés au plomb. La grande réversibilité des courbes d'aimantation en fonction du champ au voisinage de T_c nous a permis d'évaluer le champ critique thermodynamique. Celui-ci conduit à un coefficient de chaleur spécifique électronique similaire à celui des composés YBaCuO.

Abstract. — In the Bi-Sr-Ca-Cu-O system, we have studied the compound with the ideal formula $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$, responsible for the superconductivity up to 110 K. The magnetic measurements reveal the presence of two phases in the samples with superconducting transitions up to 80 K and 110 K. By varying the composition and the thermal treatment of those samples, we have succeeded in increasing the amount of the superconducting phase with T_c up to 110 K. The Meissner effect reaches 30 % of $-3/8 \pi$ at 90 K for the undoped samples and more than 50 % for the samples doped with Pb. Because of the high reversibility of the magnetization *versus* magnetic field around T_c , we have evaluated the critical thermodynamic field. This one gives an electronic specific heat coefficient similar to the one of YBaCuO compounds.

Introduction.

A few time after the discovery of superconductivity below 20 K in the Bi-Sr-Cu-O system [1], Maeda *et al.* reported a bulk superconductivity up to 85 K and the presence of traces of superconductivity up to 110 K in the Bi-Sr-Ca-Cu-O system [2].

The $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ compound was rapidly identified as the 85 K-superconducting phase [3, 4]. The formula $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ was proposed for the 110 K-superconducting phase by Tarascon *et al.* who succeeded in isolating a small crystal [5]. These compounds belong to a family of general formula $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_x$. When $n = 1$, $T_c = 20$ K ; when $n = 2$, $T_c = 85$ K ; and when $n = 3$, $T_c = 110$ K.

However, the 110 K-superconducting phase is found to be hard to stabilize : no single-phased compounds have been obtained. Up to now this last phase only appears in some samples and in very small amounts. Before studying the physical properties of this phase, we thought it was necessary to increase its amount.

The measurement of the Meissner effect at 90 K has been used to evaluate the amount of the 110 K superconducting phase in our samples. By varying the nominal composition and the thermal treatments of the samples, we succeeded in raising it from 1 % to 15 %, then 30 % and finally 52 % of $-1/4 \pi (1 - n)$ where n , the demagnetization coefficient is assumed to be 1/3, corresponding to an assembly of independent spherical particles.

Undoped samples.

Different compositions were obtained by solid-state reactions of Bi_2O_3 , CuO, SrCO_3 et CaCO_3 powders mixtures. The powder mixtures are calcinated under air, 24 hours at 800 °C. After grinding and pressing the calcinated powders into pellets, different heat treatments are applied. We obtained the following results :

a sample (A) with nominal composition $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ was heated 15 days at 800 °C, followed by natural cooling of the furnace to the

room temperature. The Meissner effect at 90 K is 6 % of $-3/8 \pi$;

a sample (B) with nominal composition $\text{Bi}_2\text{Sr}_{1.5}\text{Ca}_{1.5}\text{Cu}_2\text{O}_x$ was heated 48 hours at 880 °C, followed by natural cooling of the furnace to the room temperature. The Meissner effect at 90 K is now 15 % ;

a sample (C) with nominal composition $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ was heated 120 hours at 870 °C, followed by a slow cooling at a rate of 50 °C/h. The Meissner effect at 90 K reaches 30 % of $-3/8 \pi$.

The measurement of the magnetization *versus* the temperature in a constant magnetic field of 10 Oe clearly reveals the presence of two superconducting phases with $T_c = 80$ K and $T_c = 110$ K (Fig. 2a). Our best samples reach 30 % of 110 K superconducting phase.

However, the X-ray diffraction pattern of these compounds corresponds to a structure with $n = 2$ in the bismuth family. But the peaks corresponding to

the $n = 3$ structure, especially the 002 peak (corresponding to $2q = 4.7$ degrees in the Fig. 1) could not be seen.

This phenomenon can be discussed as follow : in our samples, the $n = 3$ phase only exists as inter-growth defects of the $n = 2$ phase. The very small extent of those defects cannot be revealed by X-ray diffraction. This result could be also related to the paper of Tarascon *et al.* who proposed that this superconducting phase grow at the surface of the grains.

Lead doped samples.

Furthermore, we noticed that the formation of the 110 K-superconducting phase was particularly sensitive to the annealing temperature. Problems of reproducibility of the annealing exist. Then we tried to introduce lead oxyde, as reported by Kijima *et al.* [6], in order to stabilize the 110 K phase.

Fig. 1. — X-rays diffraction patterns of samples (C) and (D) : a) the X-rays pattern of sample (C) corresponds to a $n = 2$ structure ; b) the X-rays pattern of sample (D) showing a major phase with 002 reflection close to 18.4 Å (4.7 degrees), corresponding to the $n = 3$ member of the bismuth family.

Fig. 2. — The zero-field cooled susceptibility (+), and the field-cooled susceptibility ($\square$), measured in a field of 10 Oe plotted *versus* temperature : a) the susceptibility of sample (C) corresponds to 30 % of superconducting volume at 90 K. The increase of the superconducting volume below 85 K is due to the « 2212 » phase ; b) the susceptibility of sample (D) corresponds to 40 % of superconducting volume at 90 K.

Samples (D) with the nominal composition $\text{Bi}_2\text{Pb}_{0.6}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+d}$ were prepared from the intimate mixture of Bi_2O_3 , PbO , CuO , SrCO_3 , and

CaCO_3 . The samples were pressed into pellets and heated in air at 800 °C for 24 hours and 870 °C for 120 hours ; the samples were then slowly cooled, at a rate of 50 °C/h to the room temperature, according to the previously reported method [6]. The X-ray analysis of the sample show evidence of a mixture, with a weak reflection corresponding to the $n = 3$ member of the bismuth family. The resistivity measurements showed a broad transition with T_c close to 77 K. The samples were then fired again at 870 °C for 65 hours and slowly cooled (50 °C/h). The X-ray pattern showed a major phase with the 002 reflection close to 18.4 Å ($2\theta = 4.7$ degrees in the Fig. 1b), corresponding to the $n = 3$ member of the bismuth family [5, 6]. We infer that in the lead doped samples, the superconductivity takes place in well-crystallized particles.

According to the Meissner effect at 90 K (Fig. 2b), the proportion of the 110 K-superconducting phase is more than 40 % and zero resistance is obtained at 105 K (Fig. 3).

The role of the lead oxide in the formation of the 110 K-superconducting phase is not clear. It seems to favour the migration of the atoms and then the ordering at lower temperatures.

Evaluation of the specific heat coefficient.

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 : $\int_0^{H_c^2} (M_s - M_n) dH = -H_c^2/8\pi$. A minimum value for this area can be

Fig. 3. — Resistivity measurements of sample (D). A zero resistance is obtained at 105 K.

extrapolated in high fields at different temperatures. The volume fraction of the sample having $T < T_c < T + dT$ is assumed to be dT/T_{co} with $T_{co} = 110$ K. This distribution leads to a linear decrease of the

Fig. 4. — Measurements of magnetization *versus* magnetic field at 100 K and 105 K of sample (C).

superconducting volume with temperature as observed in figure 2a. If the thermodynamical critical field is assumed to vary as $H_c = H_0(1 - (T/T_c)^2)$, there is a simple relation between the specific heat coefficient g , T_c and $H_0^2 = 2 \pi g T_c^2$. Assuming that the particles of the distribution have the same g but different T_c 's, we can calculate using this distribution the mean square of H_c : $H_c^2 = 2 g / T_{co} (T_{co}^3/3 - 2 T^2 T_{co} - T^4/T_{co}^4 + 8/3 T^3/T_{co}^3)$. We have determined a minimum of H_c^2 at different temperatures, and deduced a minimum g value of about 30 mJ/mole.K² using the magnetization curves *versus* magnetic field obtained at 100 K and 105 K (Fig. 4). This value is of the same order of magnitude than the value deduced from the study of the thermodynamical critical field in a sample containing about 1 % of the 110 K phase [7].

Conclusion.

We have progressively increased the fraction of the superconducting phase $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ in the Bi-Sr-Ca-Cu-O system by annealing at different temperatures and increasing the time of annealing below the melting temperature. A zero resistivity is observed below 105 K and a Meissner effect of about 40 % attributed to the 110 K phase is obtained below 100 K. The calculation of thermodynamic critical field from the reversible $M(H)$ curve allows us to evaluate the electronic specific heat coefficient which appears to be larger than 10 mJ/mole.K².

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