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Electron diffraction studies of the incommensurate modulations in (Bi-Pb)-Sr-Ca-Cu-O superconductors

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Résumé. — Nous avons étudié les modulations incommensurables dans les supraconducteurs sans plomb Bi-Sr-Ca-Cu-O, et substitués au plomb (Bi-Pb)-Sr-Ca-Cu-O à différentes températures entre 110 K et 300 K. Dans cet intervalle de température, les modulations sont indépendantes de la température. Les modulations incommensurables de deux composés substitués au plomb, de compositions nominales $\text{Bi}_{1.8}\text{Pb}_{0.2}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ et $\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ ont été observées à la température ambiante. L'amplitude de la modulation décroît quand la concentration en plomb augmente.

Abstract. We have studied the incommensurate modulations of lead free Bi-Sr-Ca-Cu-O and lead substituted (Bi-Pb)-Sr-Ca-Cu-O superconductors at different temperatures between 110 K and 300 K. The modulations are temperature independent in this interval. The incommensurate modulations of two lead substituted compounds of nominal compositions $\text{Bi}_{1.8}\text{Pb}_{0.2}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ and $\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ have been observed at room temperature. The Pb modulation value decreases with a higher lead concentration.

Introduction.

This paper deals with electron diffraction studies of the incommensurate phase of high T_c superconductors of the Bi-Sr-Ca-Cu-O and (Bi-Pb)-Sr-Ca-Cu-O systems. Following the discovery [1] of the high T_c superconductors belonging to the bismuth cuprates family, numerous studies [2-6] have been devoted to the determination of the structural symmetry of these compounds. Two main phases labeled (2212) and (2223) corresponding to the molar

ductivity respectively below 75 K and 110 K. These phases show a basic structure of orthorhombic symmetry [4] with lattice parameters $a = b = 5.4 \text{ \AA}$, $c = 30.8 \text{ \AA}$ and $a = b = 5.4 \text{ \AA}$, $c = 37 \text{ \AA}$ respectively. From diffraction experiments [4-6], there appears to be a general consensus that the space group of the average structure is Bbmb. An interesting feature is the existence of incommensurate superlattice structure [7, 8] with the wavevector $q = \delta b^* + c^*$ ($\delta = 0.21$). It has been observed [9] that the substitution of lead to bismuth increases the

proportion of the (2223) phase in ceramics and preserves the space group [10] of the basic structure and the incommensurability of the lead free compound, but induces a new incommensurate superlattice structure [11, 12] with a wavevector $q' = \delta' b^*$. Although several studies [10-14] have been devoted to the determination of incommensurate modulations in lead substituted compounds, the experimental results are relatively diversified and require to be confirmed. On the other hand, very few experiments [15] concern the temperature behavior of the incommensurate superstructure.

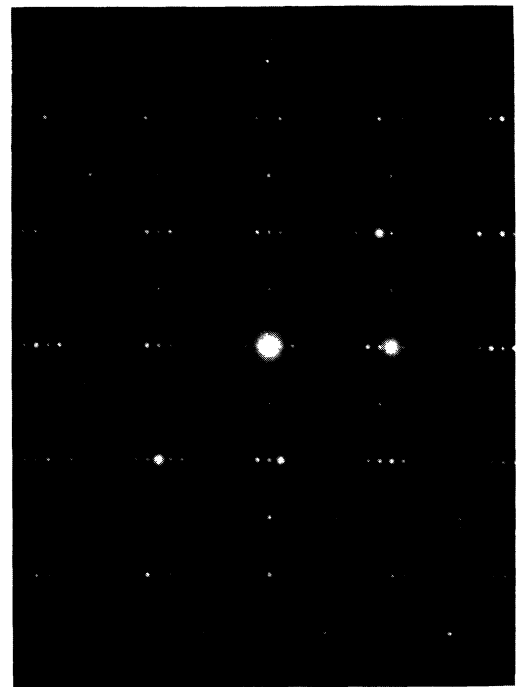
Experimental.

In this work, investigations by electron diffraction have been made on lead free compound of nominal composition $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$, and lead substituted compound of formula $\text{Bi}_{1.8}\text{Pb}_{0.2}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ at different temperatures between about 110 K and 300 K, and the temperature dependence of the magnitude of the incommensurate modulation has been determined. Some lead substituted ceramics

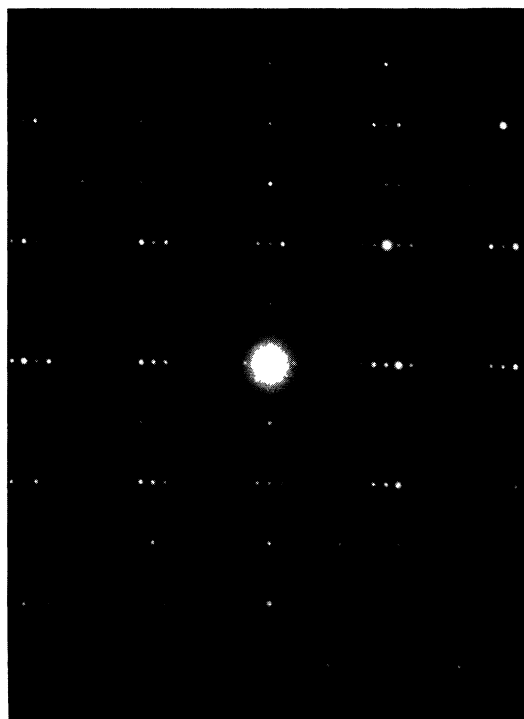
have been observed at room temperature in order to examine the modification in the incommensurate modulation wavevector by the substitution of lead. For transmission electron microscopy and electron diffraction, the samples were obtained by crushing a ceramic and depositing grains on carbon support grids. The ceramics have been prepared by taking bismuth, copper oxide and strontium and calcium carbonates, the carbonates were calcined at 1 250 °C, mixed to the other elements for reaction and sintering between 850 °C and 880 °C [16]. A Philips EM 301 and a Jeol 2000 electron microscopes with a cooling holder, using liquid nitrogen and a temperature control and measuring unit, were used for room and low temperature experiments respectively.

Results and discussion.

The electron diffraction patterns of nominal composition $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ have been obtained at about 110 K, 173 K, 223 K and 300 K (Fig. 1). The magnitude of the incommensurate modulation δ of the wavevector $q = \delta b^* + c^*$, shows an independent temperature behavior which confirms the recent work of Takenaka *et al.* [15], the estimated value of δ is 0.215 ± 0.003 (Fig. 2). For lead substituted compounds, the situation seems to be more complex. On a grain of ceramic of nominal composition $\text{Bi}_{1.8}\text{Pb}_{0.2}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$, two sets of incommensurate satellites with modulations $\delta = 0.23$ and $\delta' = 0.15$ (Fig. 3), have been observed at different temperatures between room temperature and 110 K, after cooling the sample at 110 K and heating up to 300 K and then recooling it to 110 K. The magnitude values of modulations are temperature independent, and no thermal hysteresis was revealed. The fact that the wavevectors of the modulations are temperature independent apparently disagree with the standard scheme for incommensurate systems [17] which involves the existence of three phases, a high symmetry normal phase, followed by an incommensurate phase in a temperature interval in which the wavevector has a temperature dependence, before looking to a rational value in a commensurate low symmetry phase. However, the situation encountered in bismuth superconductors is somewhat different due to the fact that the high symmetry phase does not seem to be realized below the melting temperature. On a ceramic sample of nominal composition $\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$, a low modulation with $\delta' = 0.11$ was observed (Fig. 4). This modulation value confirms the fact that in lead substituted systems, the modulation decreases as lead concentration increases [13] (Fig. 5). The fact that the higher modulation was not revealed, is probably due to the diffraction geometry of the sample. Finally, a ceramic with a high proportion of the (2223) phase (more than



a)



b)

Fig. 1. — [001] zone axis electron diffraction pattern of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$. (a) and (b) are obtained at about 110 K and 300 K respectively. The set of incommensurate satellites corresponds to a wavevector $q = \delta b^* + c^*$.

90 %) has shown the existence of grains with modulation values $\delta_1 = 0.23$, $\delta'_1 = 0.14$ and $\delta_2 = 0.21$, $\delta'_2 = 0.10$ which probably reflects the inhomogeneity in lead concentration of the ceramic, and denotes no drastic difference in the incommensurate structure of the (2212) and (2223) phases.

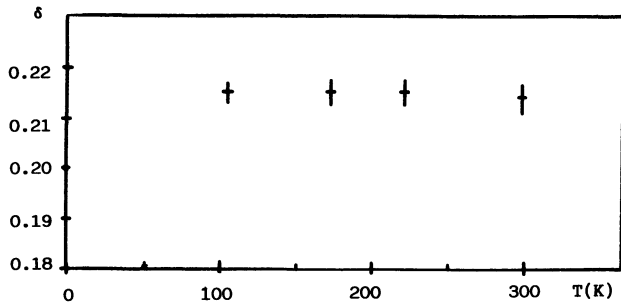


Fig. 2. — Temperature dependence of the magnitude of the incommensurate modulation δ .



Fig. 4. — [001] zone axis electron diffraction pattern of $\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$. Only one set of incommensurate satellites appears which corresponds to a wavevector component along b^* ($\delta' = 0.11$).



Fig. 3. — [001] zone axis electron diffraction pattern of $\text{Bi}_{1.8}\text{Pb}_{0.2}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$. Two sets of incommensurate satellites correspond to two wavevectors $q = \delta b^* + c^*$ ($\delta = 0.23$) and $q' = \delta' b^*$ ($\delta' = 0.15$).

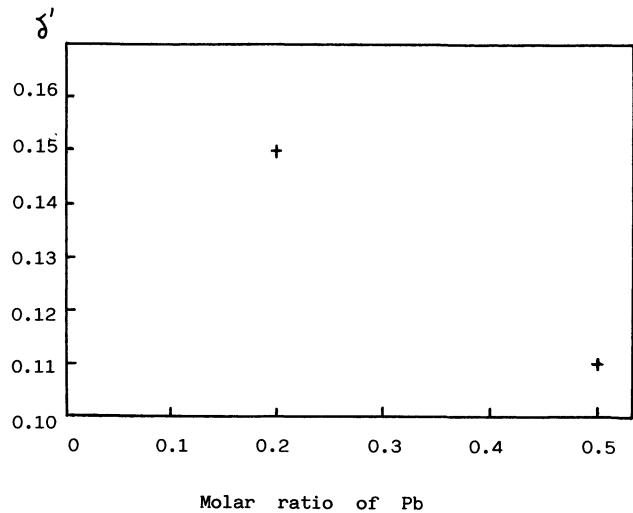


Fig. 5. — Dependence of the magnitude of the incommensurate modulation δ' with the lead concentration.

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