Intermodulation of the two incommensurate waves in $Bi_{2-x}Pb_xSr_2CaCu_2O_y$ superconducting crystals

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(Received 7 August 1989)

X-ray precession experiments on $Bi_{1.75}Pb_{0.25}Sr_2CaCu_2O_y$ single crystals show that, beside the previously reported incommensurate satellites at $q_1=\delta_1 b^*+c^*$ and $q_2=\delta_2 b^*$, there are reflections at (q_1+q_2) and (q_1-q_2). This result shows that lead addition in (2:2:1:2) bismuth compounds can induce, homogeneously in the crystal, a doubly modulated (q_1,q_2) state corresponding to an intermodulation of the two incommensurate waves with wave vectors q_1 and q_2.

It is now well established that the superconducting compounds of general formula $Bi_2Sr_2Ca_nCu_{1+n}O_{6+2n}$ (usually labeled 2:2:n:n+1) exhibit an incommensurate modulation (type I) along the b_0 direction of the orthorhombic multiple cell of their basic structure ($a_0=b_0=5.4$ Å, $c_0=24$, 30.6, or 37 Å, respectively, for $n=0$, $n=1$, and $n=2$). The wavelength of this modulation is $(1/\delta_1)\approx 4.7b_0$.[1]

It has been recently reported, on the basis of electrons and x-ray diffraction experiments,[2-5] that the addition of lead in these materials induces a second type of modulation (type II) along the b_0 direction with a longer wavelength, varying from $(1/\delta_2)\approx 6.5b_0$ to $(1/\delta_2)\approx 8.5b_0$ depending on the lead content. Another significant difference between these two modulations lies in the characteristics of their wave vector. In addition to its incommensurate component along the b^* reciprocal axis, the wave vector of the type-I modulation has a commensurate component along the c^* reciprocal axis while the wave vector of the type-II modulation has no commensurate component.

Most of the x-ray and electron-diffraction patterns[2-5] of lead-containing compounds show that the satellites of both incommensurate modulations coexist in reciprocal space. However, Ikeda *et al.* have observed[2] that the satellite spots corresponding to the type-I modulation become diffuse as the lead content increases. From this observation, these authors have concluded that type-II modulation should become the stable modulation as lead is added, and that the coexistence of the two modulations in the same sample should be a metastability effect. Consistently, some samples, corresponding to high lead concentration, displaying only the type-II modulation have been observed in electron-diffraction experiments.[6]

However, until now it has not been clarified whether the two modulations, when they coexist, are spatially separated or locally superimposed to form an ordered homogeneous state. In this respect, high-resolution electron-microscope experiments have shown a variety of situations. Chen *et al.*[4] have reported that the two modulations are generally realized in distinct regions, but that they can sometimes be superimposed in small domains situated near the boundaries of the preceding regions. Ikeda *et al.*[2] have mainly observed regions with disturbed periodicity which cannot be unambiguously interpreted either as resulting from a local interaction of the two modulations, or from fluctuations in the distribution of lead. Finally, Hewatt[7] has observed that superimposition of the two modulations occurs at the scale of a few hundred angströms.

By means of an x-ray precession investigation of lead containing single crystals of the 2:2:1:2 phase, we show, for the first time, that the addition of lead can induce an ordered homogeneous doubly modulated state resulting from a superimposition and an interaction in real space of the type-I and type-II modulations. This is shown by the observation of well defined reflections at positions corresponding to the sum and the difference of the wave vectors of those two modulations. In this paper, we report the x-ray studies which demonstrate the existence of this doubly modulated state and we discuss its consequences on the understanding of the incommensurate properties of the lead substituted Bi-Sr-Ca-Cu-O compounds.

Single crystals of the 2:2:1:2 phase were elaborated by a method described elsewhere[5] which consists in slowly cooling melts of composition $(Bi_{2-x}Pb_xSr_2CaCu_2O_{8-x/2}+7CuO)$ after maintaining them near 950 °C. We present here results relative to crystals which are extracted from a melt corresponding to $x=0.5$. Chemical analyses by means of an electron microprobe, of micrometer diameter, have been undertaken on several crystals. They indicate for each investigated sample a uniform composition over the surface. The approximate formula of the different crystals has been determined as $Bi_{2-x}Pb_xSr_2CaCu_2O_y$ with $0.22<x<0.25$. X-ray precession investigations have been effected by using a monochromatic radiation (Mo $K\alpha$, $\lambda\approx 0.709$ Å).

The photograph of the $(0kl)$ reciprocal plane represented in Fig. 1 exhibits several types of reflections. Some of these reflections have previously been observed and reported.[5] These are as follows: (i) the "main" reflections consistent with the orthorhombic basic structure with lattice parameters $a_o\approx b_o\approx 5.4$ Å and $c_0\approx 30.6$ Å; (ii) the incommensurate satellites reflections, corresponding to type-I and type-II modulations, with respective wave vectors $q_1=\delta_1 b^*+c^*$ and $q_2=\delta_2 b^*$; (iii) second-harmonics reflections at $2q_2$. In addition, new incommensurate reflections are observed for the first time. They are situated at positions corresponding to the combinations (q_1+q_2) and (q_1-q_2). This has been established by means

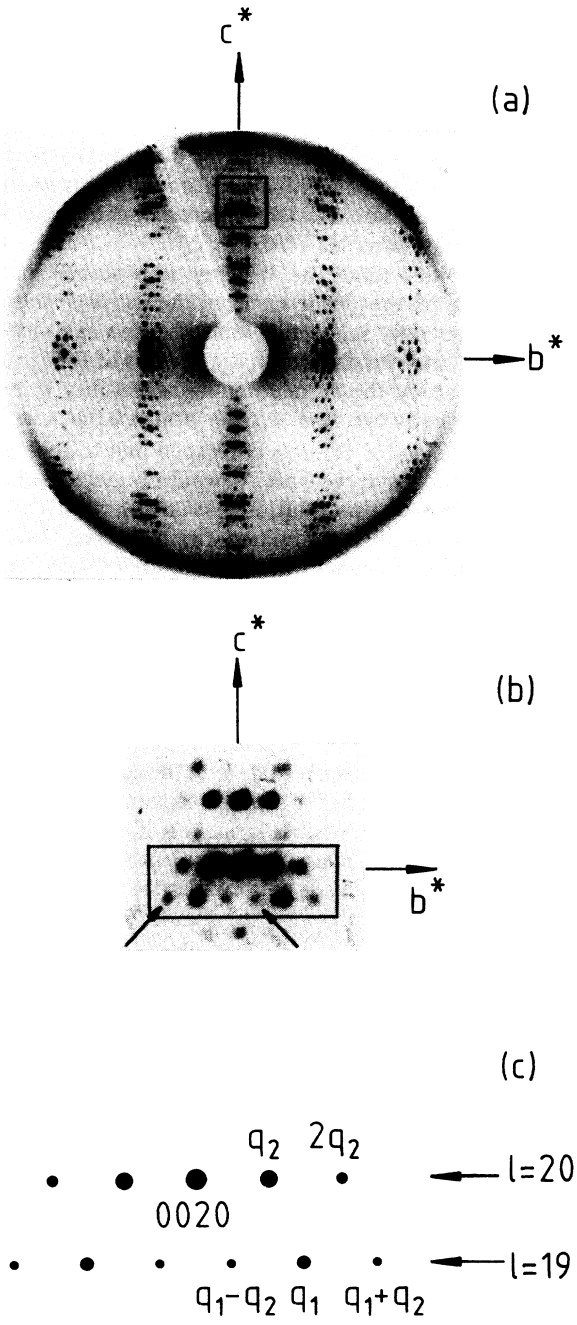

FIG. 1. (a) Precession photograph of the $(0kl)$ reciprocal plane. (b) Enlargement of the framed region in photograph (a). New incommensurate reflections are indicated by arrows. (c) Schematic representation of the diffraction pattern situated inside the framed region of (b), showing the identification of the different reflection spots.

of microdensitometer scans along the b^* direction for different fixed values of l. Two characteristic scans are represented in Fig. 2. One corresponds to $l=2n$ (here $l=20$); it scans a reciprocal line which contains main Bragg reflections $[0,2m,2n]$ (here [0,0,20]), and incommensurate satellites at $\pm q_2$ and $\pm 2q_2$. The other one corresponding to $l=2n+1$ (here $l=19$) scans a reciprocal

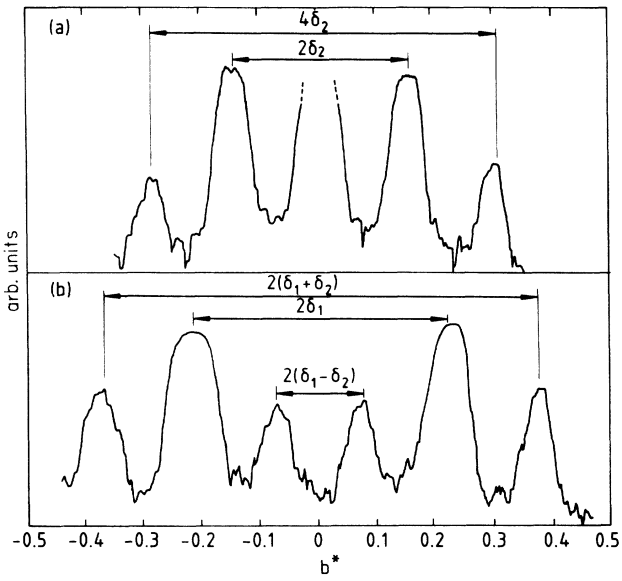

FIG. 2. Microdensitometer scans along the b^* direction of the two reciprocal lines $l=19$ and $l=20$. (a) $l=19$; scan of the satellites with the wave vectors $\pm q_2$ and $\pm 2q_2$. (b) $l=20$; scan of the satellites with the wave vectors $\pm q_1$, $\pm(q_1+q_2)$, and $\pm(q_1-q_2)$.

line which contains the incommensurate satellites at $\pm q_1$ and the newly observed incommensurate reflections. The values of $\delta_1=0.220\pm0.003$ and $\delta_2=0.152\pm0.002$ have been deduced from these microdensitometer measurements. The wave vector of the new incommensurate reflections have also been quantitatively determined as $(0.073\pm0.002)b^*+c^*$ and $(0.376\pm0.003)b^*+c^*$, and consequently identified as $q_1-q_2=(\delta_1-\delta_2)b^*+c^*$ and $q_1+q_2=(\delta_1+\delta_2)b^*+c^*$.

We have carefully checked that these reflections do not have their origin either in multiple scattering or in the second harmonic of the wavelength of the x-ray radiation. Hence, these (q_1-q_2) and (q_1+q_2) reflections are still observable if either the geometry of diffraction is changed [for example, by taking photographs of the $(hk1)$ reciprocal plane], or if the harmonics of the radiation are suppressed by applying to the x-ray tube a voltage below the excitation potential for $\lambda/2$. Moreover, the existence of these reflections has been established for several samples.

Our results clearly show that, in the investigated samples, type-I and type-II modulations cannot be considered as independent. In real space, they locally interact and produce the observed intermodulation of the two incommensurate q_1 and q_2 waves. We can therefore infer that a doubly modulated (q_1,q_2) homogeneous state exists in the crystal. It is worth noting that the widths of the newly observed incommensurate reflections are comparable to the one of the Bragg reflections, thus showing that the (q_1,q_2) state is spatially ordered. However, we have noted that the existence of the (q_1-q_2) and (q_1+q_2) reflections does not seem to occur for all values of lead substitution. In the first place, previous x-ray and electron-diffraction experiments, with sensitivities comparable with ours, did

not mention such observations.[2-5] In the second place, our own x-ray diffraction experiments have disclosed these reflections only for crystals corresponding to the composition mentioned in this paper, while these reflections were checked to be absent for other compositions. Moreover, measurements for single crystals containing more lead, which will be reported elsewhere,[8] confirm the observation of Ikeda *et al.*[2] that the type-I incommensurate satellites become very weak and diffuse while the type-II satellites remain intense and well defined. Consequently, it is probable that the occurrence of a doubly modulated (q_1,q_2) state can take place only in a limited range of lead concentrations, and that for higher lead concentrations the type-II modulation alone is stable while the type I is metastable. This would explain the variety of results reported from high-resolution transmission-electron-microscopy observations. In particular, the results of Ikeda *et al.*[2] and Hewatt[7] might correspond to samples presenting the (q_1,q_2) state, though these results are not clear enough to specify the arrangement in real space of the interacting type-I and type-II modulations.

This interaction of the two modulations cannot be simple. Indeed, it is now accepted that the most significant difference between the type-I and type-II modulated structures lies in different stacking modes along the c_0 direction, of perovskitelike wafers, limited by Bi-O planes.[9] Each of these wafers is modulated incommensurably along b_0, the modulation consisting primarily (but not only) in atomic motions within the Bi-O planes.[10] The commensurate component of q_1 along c^* has been shown to result from an out-of-phase stacking of consecutive wafers, while an in-phase stacking is consistent with the absence of commensurate component for q_2.[9] At present, it is not clear how the two modulations can mix in real space, in a way compatible with their respective structural description, to form the (q_1,q_2) state. In particular, we cannot say whether this state corresponds to a superimposition of the two types of stackings, or if the very structure of the wafers is affected. This point should be clarified by further high-resolution electron-microscopy observations in the appropriate samples.

A feature which might be of prime importance for the understanding of the occurrence of the (q_1,q_2) state in certain samples only is the fact that in these samples the wavelength of the two characteristic periods of the (q_1,q_2) state nearly satisfy the simple commensurability relation $\delta_1/\delta_2=\frac{3}{2}$; actually we find $\delta_1/\delta_2=1.45\pm0.04$. As this relation only holds for crystals corresponding to the range of composition considered here, it would be interesting to investigate whether this relation has a link with the occurrence of the doubly modulated (q_1,q_2) state. For example, a local arrangement of the two modulations could be favored, when these are commensurate with each other (though both incommensurate with the underlying lattice).

In conclusion, our studies have specified the influence of lead on the types of incommensurate modulations existing in $Bi_{2-x}Pb_xSr_2CaCu_2O_y$ superconducting crystals. In particular we have shown that a homogeneous (q_1,q_2) modulated state is stable for a range of lead concentration around $x=0.25$. The possible influence of the presence of this doubly modulated phase on the superconducting properties of these compounds is under investigation.

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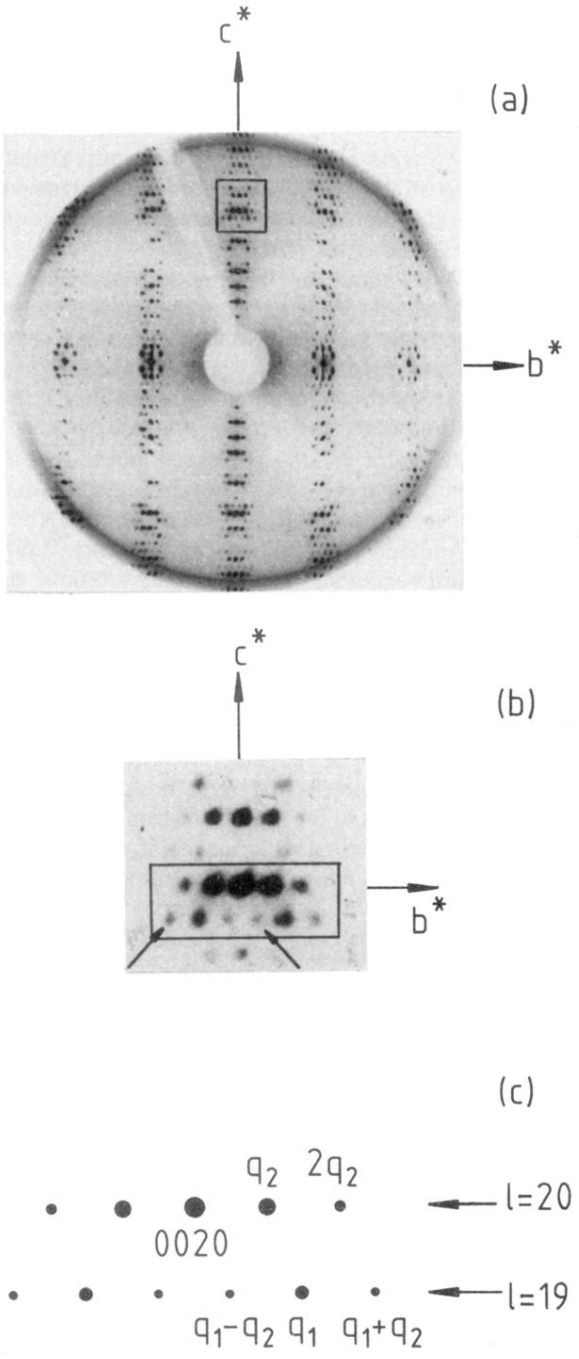

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