

Space symmetry of the basic structure and incommensurate modulations in $(\text{Pb,Bi})_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ superconductor single crystals

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Lead-containing single crystals of the (2:2:1:2) phase have been studied on the basis of monochromatic x-ray precession camera investigations. Compared to the lead-free compound it is shown that the lead addition only affects the incommensurate properties preserving the space symmetry of the basic structure. The presence of two incommensurate modulations is pointed out, consistent with recent results, and their characteristics are specified. The type of modulation which also exists in the lead-free compound has its wavelength and its anharmonicity reduced by the lead addition. The other modulation is specific of lead-containing compounds and has the wave vector $(0, \frac{1}{8}, 0)$. These results suggest that the lead atoms substitute in part the Bi atoms in the Bi-O layers of the structure.

Recently there has been intense activity in the elaboration and study of lead-containing Bi-Sr-Ca-Cu-O superconducting ceramics. This effort has been stimulated by the observation that lead addition favors the formation of a phase which is superconducting, below 107 K with respect to the formation of a phase with a lower T_c (≈ 75 K).¹⁻⁶ In lead-free ceramics the corresponding two phases have respectively been labeled (2:2:2:3) and (2:2:1:2) consistent with their ideal chemical formula $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ (Ref. 7) and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ (Ref. 8). Up to now neither the precise chemical composition nor the structure of the phases present in the lead-containing ceramics are known. In particular, the role of lead in the stabilization of the "higher T_c " phase and its influence on the physical properties of this phase have not been clarified. Very recently we were able to show on the basis of local chemical analysis of the grains of the ceramics, as well as of the single crystals of the (2:2:1:2) phase, that lead is effectively introduced in the structure of the superconducting material.⁵

In this paper we have studied, on the basis of single-crystal x-ray precession experiments, the structural modifications which are experienced by the (2:2:1:2) phase and which give additional evidence of the penetration of lead in the very structure of the compound. These results are a step in the clarification of the role of lead at the microscopic level. Recently electron microscopy and x-ray studies have shown that there is some specific incommensurate modulation related to the introduction of lead.^{9,10} In the present study we have obtained x-ray precession pictures of lead-containing (2:2:1:2) single crystals by using a monochromatic radiation (Mo $K\alpha \approx 0.709$ Å). This method avoids spurious streaks generally observed with x-ray-filtered radiations or multiple reflections coming from electron diffraction experiments, and allows the reliable determination of the systematic allowed reflections as well as the observation of weak superlattice spots. We confirm the existence of a modulation characteristic of the lead-containing compound and we specify the characteristics of this modulation compared to the one of the lead-free compound. Furthermore, we point out

that the space group of the average structure is not affected by the lead addition. These results are discussed in the light of structural data available for the lead-free compound.

Single crystals were elaborated by slowly cooling melts of composition $(\text{Bi}_{0.6}\text{Pb}_{0.4}\text{Sr}_2\text{CaCu}_2\text{O}_{7.8} + 7\text{CuO})$ after maintaining them for 12 h at $\sim 950^\circ\text{C}$. Crystal wafers, perpendicular to the c axis of approximately 1 mm lateral size and a few tens microns thick could be extracted from the solidified melts. Chemical analysis by means of an electron microprobe yielded a uniform composition over the surface (at one micron scale) corresponding to the approximate formula $\text{Bi}_{1.4}\text{Pb}_{0.6}\text{Sr}_{1.5}\text{Ca}_1\text{Cu}_{1.7}\text{O}_x$.

Owing to the relative complexity of the results obtained in the lead-containing crystals, it is relevant to refer these to those known at present for the crystallographical characteristics of the lead-free (2:2:1:2) phase.

In a first approximation the structure of the (2:2:1:2) phase can be considered as tetragonal (space group $I4/mmm$). The elementary unit cell contains one formula, while the standard multiple tetragonal cell, with lattice constants $a_t = b_t = 3.8$ Å and $c_t = 30.8$ Å contains two formulas.⁸ The structure is actually orthorhombic with a and b lattice vectors rotated by 45° around c , with respect to the corresponding tetragonal lattice vectors. Referring the set of Bragg reflections of the space group $I4/mmm$ to the orthorhombic frame of reference, one obtains a pattern of spots which can be assigned to the $Fmmm$ orthorhombic space group.¹¹ Since this assignment is only a relabeling of the above tetragonal space group the elementary unit cell of the corresponding structure still contains one formula. However, the standard multiple orthorhombic cell, with lattice constants $a_0 \sim b_0 \sim 5.4$ Å, $c_0 \sim 30.8$ Å contains four formulas.

Refined x-ray or electron diffraction experiments have revealed, in addition to the former Bragg reflections, that the presence of two types of weak superlattice reflections determine a more complex symmetry.

First there is a set of commensurate superlattice spots. Their presence determines a lower translational symmetry than that of the $Fmmm$ space group. On their basis the

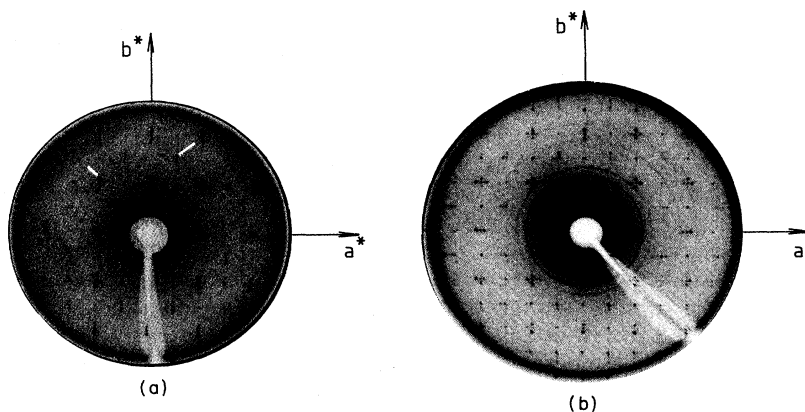


FIG. 1. (a) Precession photograph of the $(hk0)$ reciprocal plane corresponding to an untwinned region. The two different types of incommensurate satellites are indicated by white arrows. (b) Precession photographs of the $(hk2)$ reciprocal plane corresponding to a twinned region. The incommensurate spots correspond to the modulation specific of the lead compound. Weak harmonics of the modulation can be observed.

structure has been assigned either the $Bbmb(D_{2k}^{20})$ space group or the $Bb2b(C_{2v}^{13})$ one.¹² In both cases the standard multiple cell remains the same as that of the $Fmmm$ group (i.e., $5.4 \times 5.4 \times 30.8 \text{ \AA}^3$), but the elementary unit cell contains two formulae.

On the other hand, there is a set of incommensurate satellite reflections which disclose the existence of an incommensurate modulation the wave vector of which is $q = \delta b^* + c^*$ with $\delta \approx 0.21$ (close to $1/5$).¹²⁻¹⁴ Thus, the modulation is incommensurate along the b^* axis. This modulation can be considered as superimposed on the basic crystalline structure having the symmetry $Bbmb$ or $Bb2b$ described here above. An important feature of this modulation is its nonsinusoidal character revealed by the presence of relatively strong satellites of higher order corresponding to harmonics of the fundamental wavelength of the modulation.^{12,14}

Finally, in addition to the two sets of superlattice spots discussed above, one sometimes observes in certain samples sets of spots generated from the preceding ones by rotation of 90° around the c axis. These spots have been assigned to the existence of "twist domains" which interchanges the a and b orthorhombic axes.¹³ This type of twinning is not fully clarified and is probably of a different nature than the one well described in Y-Ba-Cu-O.¹⁵

Let us now describe the results obtained in our lead-containing crystalline samples. In the first place we observe diffraction spots which are close analogs of the ones found in the lead-free phase.

Thus, the precession pictures of the $(hk0)$, $(hk2)$, and $(0kl)$ (Figs. 1 and 2) reciprocal planes of lead containing crystals exhibit main reflections which are consistent with the $Fmmm$ symmetry with lattice parameters $a_0 \approx b_0 \approx 5.4 \text{ \AA}$ and $c_0 \approx 30.8 \text{ \AA}$. Sets of commensurate and incommensurate superlattice spots are also observed. Moreover, the photographs of the $(hk0)$ and $(hk2)$ plane show the presence of twinning in the sample (Fig. 1): When the beam probes uniform regions the picture shows superlattice spots corresponding to an asymmetry between

the a and b directions, while a probing in twinned regions shows an apparent tetragonal symmetry, the a and b directions being interchanged in consecutive domains. This is the same type of twinning as the one observed in lead free compounds.^{13,14} This twinning has to be taken into account in the interpretation of the photographs.

Let us first consider the commensurate superlattice spots which define together with the $Fmmm$ main Bragg

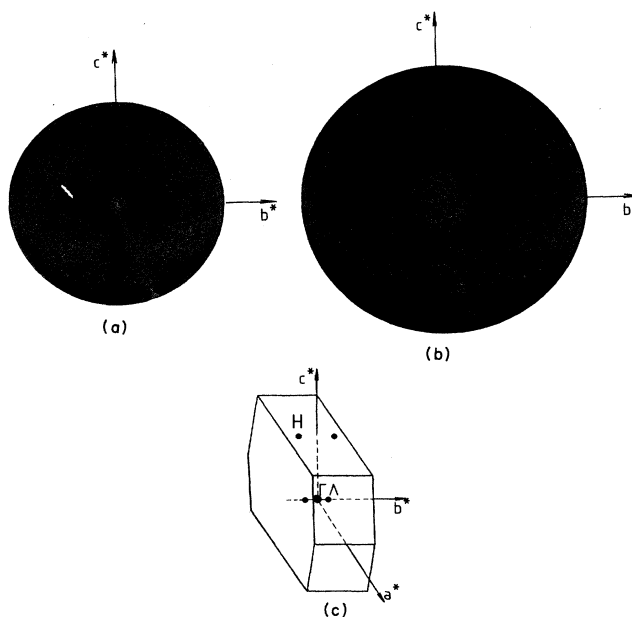


FIG. 2. (a) Precession photograph of the $(0kl)$ reciprocal plane. The two different types of incommensurate satellites are indicated by white arrows. The larger one indicates the satellites specific of lead-containing crystal. (b) Precession photograph of the $(1kl)$ reciprocal plane. (c) Brillouin zone of the B face centered lattice. The two types of incommensurate satellites respectively correspond to the H and Λ points.

reflections the diffraction pattern of the "basic" commensurate structure. Investigation of the $(hk0)$ reciprocal planes [Fig. 1(a)] corresponding to an untwinned region shows reflections at position $(2n+1)a^* + nb^*$. However, photographs of the $(0kl)$ reciprocal planes (Fig. 2) allow us to specify their positions along the c^* direction as being $(2l+1)c^*$. Accordingly, the observation of these commensurate superlattice spots in the $(hk0)$ plane are the result of a lack of resolution along c and of the consequent contamination of the $l = \pm 1$ levels, due to the smallness of the c^* parameter. We can conclude that the actual locations of the commensurate superlattice spots are $(2n+1)a^* + nb^* + (2l+1)c^*$. Hence the basic structure has a symmetry defined by a reflection condition $h+l=2n$ which is characteristic of a B face-centered orthorhombic space group. In order to further specify this space group we have examined the systematic extinctions for the main and commensurate superlattice reflections in the reciprocal planes $(hk0)$, $(0kl)$, and $(1kl)$ (Figs. 1 and 2). For this purpose the voltage applied to the x-ray tube was occasionally below the excitation potential for $\lambda/2$ in order to avoid contamination of the photographs by harmonics of the radiation used. We found in the $(hk0)$ picture corresponding to an untwinned region the possible reflections $h=2n, k=2n$. If we assume that the $(0kl)$ and $(1kl)$ pictures correspond to untwinned samples, no satisfactory match is obtained between the systematic extinctions and any of the B orthorhombic space groups. By contrast, by taking into account a twinning (interchange of h and k), we were able to assign the permitted reflections conditions $(0kl); k=2n, l=2n; (h0l); h+l=2n;$ which determines the same possible space group ($Bbmb$ or $Bb2b$) than those assigned to the lead-free compound.

Let us now focus on the incommensurate spots. We can deduce from the $(hk0)$ picture [Fig. 1(a)] corresponding to the untwinned region, that the incommensurate spots, surrounding the Bragg spots of the basic structure, are lined up along the b^* direction. Remarkably there are two different spacings between consecutive satellites. The first one is consistent with a modulation wavelength close to $5b$ as in the lead-free compounds.¹²⁻¹⁴ The second one is consistent with a larger modulation wavelength close to $7b$.

The $(0kl)$ and $(1kl)$ pictures allow a more complete characterization of the two sets of incommensurate satellites. The first set consists of spots situated at the H point of the surface of the first Brillouin zone corresponding to the basic structure, with the wave vector $\delta b^* + c^*$ (Fig. 2) [accordingly their observations in the $(hk0)$ plane also results from a contamination coming from the $l = \pm 1$ levels]. The wave vector differs from the one found in the lead-free compound by the magnitude of δ , i.e., $\delta=0.23$ instead of 0.21. Another important difference is that in contrast with the lead-free compound we do not observe here harmonics of the modulation

The second set of incommensurate satellites consists of

spots situated at the Λ point inside the Brillouin zone with the wave vector δb^* , and is specific of lead-containing crystals. A similar observation was recently reported.^{9,10} However, we obtain a larger value for δ (0.155 instead of 0.12). This discrepancy might be related to a difference in lead content, which was not specified in Ref. 9, in the investigated crystals. For this second set of incommensurate satellites we observe in the $(hk2)$ reciprocal plane weak harmonics of the modulation [Fig. 1(b)].

It has been recently noticed that in the lead-free compounds the modulation should be of the displacement type.¹⁴ This statement derives from the observation that there is no detectable incommensurate satellites around the $(h0l)$ main reflections while there are intense ones around $(0kl)$. Actually this strong asymmetry seems to rule out a modulation of concentration because in that case the relative intensity of the satellites with respect to the main reflections should be the same for each reflection. This argument still holds for lead containing compounds because we also observed this asymmetry for both types of incommensurate satellites (Fig. 1).

Our results have shown that the lead addition only affects the incommensurate properties, preserving the basic structure of the lead free compounds. Thus the modifications induced by the lead addition on the refined structure have to be understood by considering the structural units which are involved in the incommensurate modulation of the lead free compound. The nature of this modulation has not been understood fully until now. However, it has been shown, on the basis of high-resolution electron microscopy¹⁶ that it essentially concerns the Bi-O layers of the structure. As the addition of lead induces both a change in the characteristics of the incommensurate modulation specific of the lead-free compounds and the appearance of a new modulation it is probable that the lead atoms are situated in the Bi-O layers substituting part of the Bi atoms. As a consequence the persistence, with some modifications, of the usual modulation could be attributed to the remaining Bi atoms and the appearance of the new one should be related to a Pb ordering.

In conclusion, it is worth stressing that the Bi-O layers are currently supposed to control the number of O electron holes and the superconducting carriers of the CuO_2 layers.^{17,18} Consequently, the replacement of some bismuth atoms by lead should induce changes in the number of holes because of charge differences between the Bi and the Pb ions, and affects the superconducting behavior. As we have shown that this substitution also greatly affects the incommensurate modulation, the characteristics of this modulation could be linked to the superconducting properties of these compounds.

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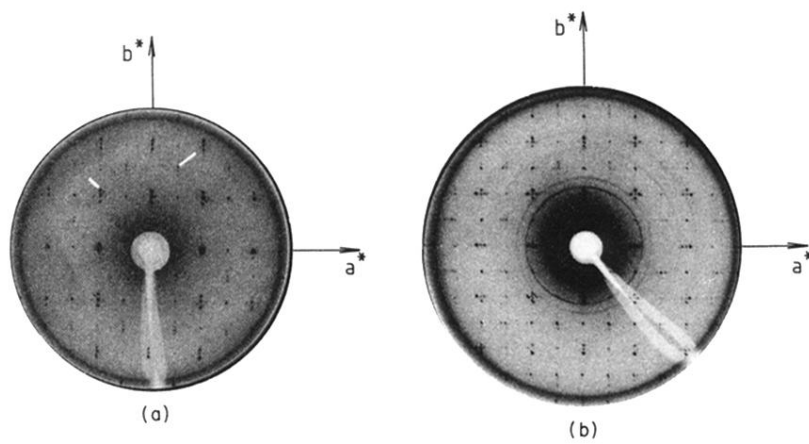


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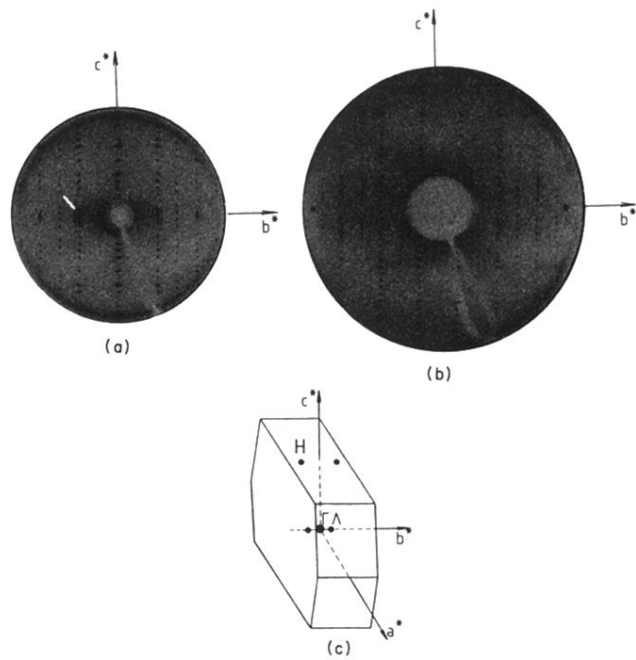


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