Growth spirals on single crystals of YBa$_2$Cu$_3$O$_{7-x}$

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Abstract
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DOI : 10.1016/0921-4534(89)904863
GROWTH SPIRALS ON SINGLE CRYSTALS OF YBa_2Cu_3O_{7-x}

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Received 27 November 1988

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1. Introduction

Since the discovery of high temperature superconducting oxides [1,2], single crystals of YBa_2Cu_3O_{7-x} (YBCO) have been grown from high temperature solutions by numerous laboratories [3]. Careful examination of the surface morphology of as-grown crystals may be helpful for elucidating the growth mechanisms of YBCO and may lead to a better understanding of its properties (anisotropies, twinning structure, etc.). In this contribution, we report the results of our recent observations on single crystals of YBCO. The occurrence of some unusual spirals is discussed.

2. Crystal growth experiments

The crystal growth experiments were performed in a muffle furnace which has been described elsewhere [4]. Preparation of YBCO single crystals was carried out as follows: YBCO powder was synthesized as a raw material by calcination of a stoichiometric mixture of Y_2O_3, BaCO_3 and CuO for 18 hours at 960°C. The calcined YBCO powder was mixed with CuO-BaCO_3 as flux in a YBCO to a flux weight ratio of 1:9. Three grams of this mixture were homogenized and pressed with 10 tons/cm^2 into a pellet of 8 mm diameter. With a view to avoiding any impurity incorporation into the crystals the pellet was put into a self-made CuO crucible, positioned on a ZrO_2 sheet in the furnace. The furnace was slowly heated from room temperature to 800°C over 6 hours, then to 1010°C at 40°C per hour, held at 1010°C for 12 hours, and slow-cooled to 900°C at 5°C per hour, then to 500°C at 35°C per hour, held at 500°C for 7 hours, then furnace-cooled to room temperature. All the experimental steps were performed in air. In some of the experiments run under these conditions, many small square platelets of YBCO (up to dimensions 2×2×0.1 mm^3) had crystallized on the exterior surface of the lower part of the crucible. So far the growth process is not yet understood, but involves of course reaction of the starting mixture with the CuO of the crucible, which roughly maintains its initial form.

3. Morphology of growth spirals

We have carefully examined as-grown crystals by means of an optical microscope. Growth steps and growth spirals were observed on a large proportion of the crystals examined. The spirals observed show clearly octagonal forms (fig. 1). In order to understand the occurrence of these unusual octagonal spirals, let us firstly consider theoretically the morphology of growth spirals of YBCO by means of the periodic bond chain (PBC) theory [5]. A detailed PBC analysis of YBCO is beyond the scope of this paper and only the results which are helpful to explain our observations are given.
In general the morphology of a growth spiral is principally controlled by the roughness of the spiral step [6]. If the step is rough, which means that the kink density is high, the step can advance independently of the crystallographic directions and the spiral will become circular. If the spiral step is smooth, which occurs when the kink density is low, the crystallographic directions become pronounced and the spiral will be more polygonized. During the growth process of a crystal, growth steps along stronger bonds contain a lower kink density than those along weaker bonds. Therefore, when a growth spiral is polygonized, the morphology is defined by the stronger bonds in the face. These stronger bonds should be consistent with the PBC directions in the face. A PBC is an uninterrupted sequence of periodically repeated strong bonds in a certain crystallographic direction [5]. By a strong bond is meant here a bond which is in the first coordination sphere of an ion, atom or molecule. Only the bonds formed during the crystal growth process are considered. A PBC must have a stoichiometric composition.

The crystal growth of YBCO occurs at a temperature above 900°C, a temperature at which the tetragonal phase is the thermodynamically stable one. The crystal structure of tetragonal YBCO is shown in fig. 2 [7-10]. For this relatively complicated structure we consider simply the "primitive PBC" which is defined as an uninterrupted periodic chain of strong bonds, disregarding the conditions of stoichiometry and electroneutrality [11]. We simplify by admitting that growth units of YBCO are simply single atoms. Therefore, all the bonds are taken into consideration for PBC analysis. For the (001) face of YBCO, two different "primitive PBCs" can be distinguished: (I) parallel \( \langle 100 \rangle \), consisting of \( \cdots -Cu_2-O_3-Cu_2-O_3-\cdots \) chains and (II) parallel \( \langle 110 \rangle \) consisting of \( \cdots -Ba-O_2-Ba-O_2-\cdots \) chains. Evidently, two PBCs can be obtained from these two primitive PBCs, respectively. The \( \langle 100 \rangle \) PBC is by far stronger than the \( \langle 110 \rangle \) PBC. Thus, if the spiral steps are smooth, the spiral on a (001) face of YBCO will be a square bounded by \( \langle 100 \rangle \) directions, the strongest PBC directions in the face. Under the condition corresponding to a higher roughness of spiral steps, the square spiral will be truncated by \( \langle 110 \rangle \) directions, the next-strongest PBC directions in the face.

![Fig. 1. Photographs showing a simple octagonal spiral (a) and the cooperation of octagonal spirals originating from neighboring dislocations (b).](image)

![Fig. 2. Crystal structure of tetragonal YBa\(_2\)Cu\(_3\)O\(_{7-x}\) with indication of the two "primitive PBC" directions.](image)
face. In this case, we obtain an octagonal spiral. While for still higher roughness of spiral steps, circular spirals would be expected.

As shown in fig. 1, the formation of the theoretically deduced octagonal spirals on (001) face of YBCO are confirmed by our observations. Square growth spirals and growth steps have been observed on (001) faces of YBCO crystals grown in Al$_2$O$_3$ crucibles both with Ga$_2$O$_3$ as dopant (fig. 3) [12] and without dopant [13]. The octagonal and square spirals obtained with CuO and Al$_2$O$_3$ crucibles, respectively, are probably due to a difference in spiral step roughness and related to the respective absence and presence of Al (Ga) impurities in the growth medium.

In conclusion, the observed morphologies of growth spirals are in good agreement with the result of our simplified PBC analysis and show that the presence of Ga and Al in the growth medium may decrease roughness of growth steps on (001) faces of YBCO.

Acknowledgements

The authors would like to thank E. Burkhardt and R. Cros for technical assistance. This work was supported by the Swiss National Science Foundation.

References