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Abstract The incommensuration of two high T_c Bi-Sr-Ca-Cu-O compounds has been investigated by electron diffraction and high resolution electron microscopy. The results suggest discommensuration rather than sinusoidal modulation of the atomic positions.

INTRODUCTION

It is generally assumed that the bismuth high temperature superconductors crystallize in structures related to Aurivillius phases with ideal compositions $Bi_2Sr_2(CaCuO_2)_{n-1}CuO_6$ (n=1, 2, and 3). The structure consists of slabs of Ca, Sr-, and Cu-oxygen layers with perovskite-like atomic arrangements separated by a double layer of Bi atoms. Adjacent slabs are shifted relative to one another by $\sqrt{2}a_p$, $\sqrt{2}a_p$, 0, resulting in a body centered cell as shown for n=2 and n=3 in Figure 1.[1] The superconducting temperature increases with n. The actual structure, however, is further complicated by the existence of a commensurate superlattice with $\bar{A}=\sqrt{2}a_p$ and $B=\sqrt{2}a_p$ and a discommensuration with $\underline{q}=0.21b^*$. A very small component of $\underline{q}$ in the a-direction is normally overlooked, but shows itself in a small rotation (less than one degree) of the strings of satellites relative

to the b axis. The satellites have been attributed to displacement modulations, substitution modulations or both.

Many nonstoichiometric Bi compounds can be formed by substitution of Sr, Cu, and Ca for Bi.[2,3] The nominal composition of our low temperature sample (n=2) is $Bi_2Sr_2CaCu_2O_x$ and for the high temperature sample (n=3) is $Bi_2Sr_{1.4}Ca_{2.2}Cu_3O_x$.

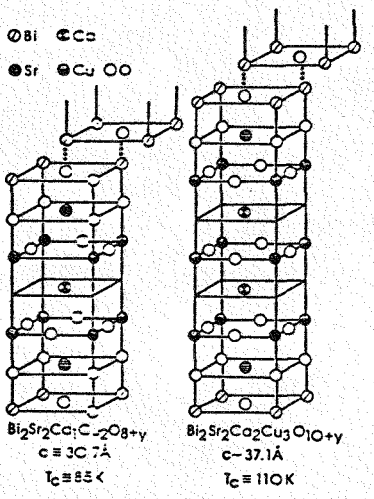

Figure 1. Aurivillius-like phases for n=2 and n=3, according to Tarascon et al.[1] with base vectors.

Results

[001] zone axis high resolution images show the modulation related to the satellites in the thicker regions of the crystal. Typically, fairly well ordered regions in narrow bands, two or three unit cells wide, are followed by wider more disordered regions, about seven unit cells wide. Especially, the stacking of the unit cells in the a-direction appears to vary, as is evident from a comparison between Figure 2a and Figure 2b. The latter shows antiphase stacking with a domain size identical to the modulation period.

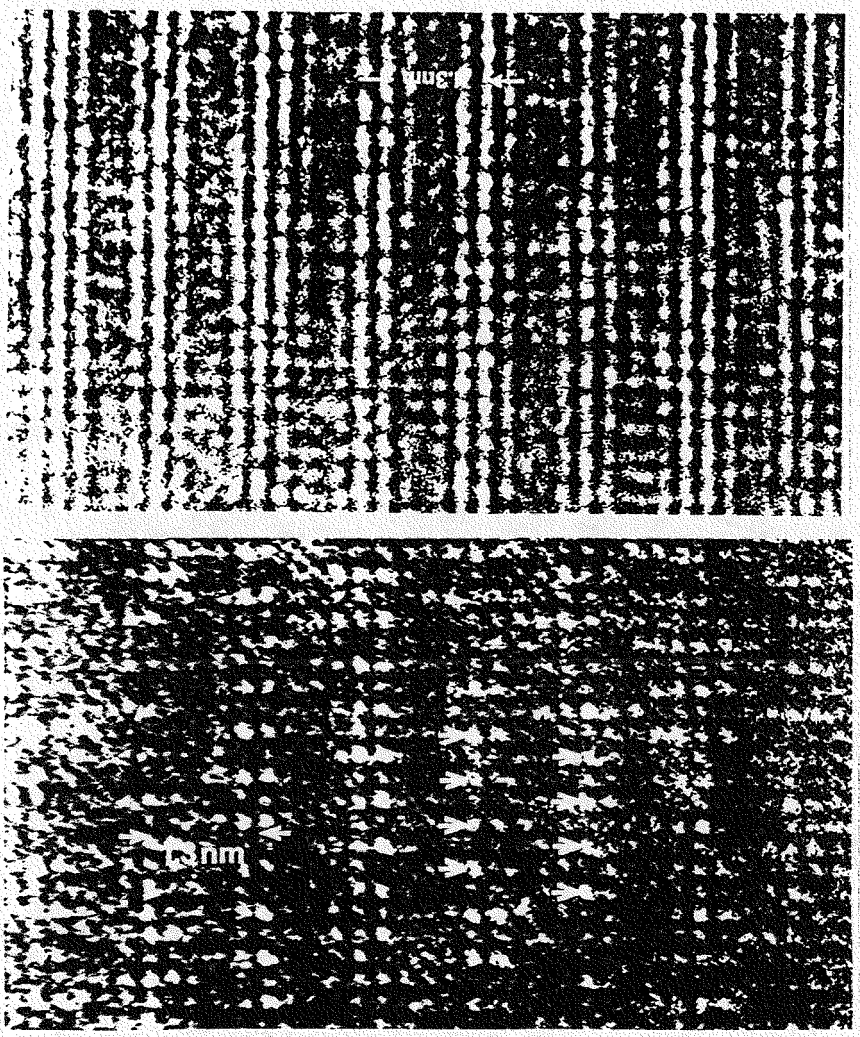

Figure 2. [001] zone axis high resolution images: a) Normal stacking of unit cells along a; b) Antiphase unit cell stacking along a with domain width of approximately 5b.

More informative high resolution patterns are obtained by tilting the crystal about the b-axis looking down h0ℓ. Figure 3a for the high T_c phase and Figure 3b for the low T_c phase show nets of columns containing equivalent atoms separated by 1/2, 1/2, 0 and -1/2, 1/2, 0 respectively.

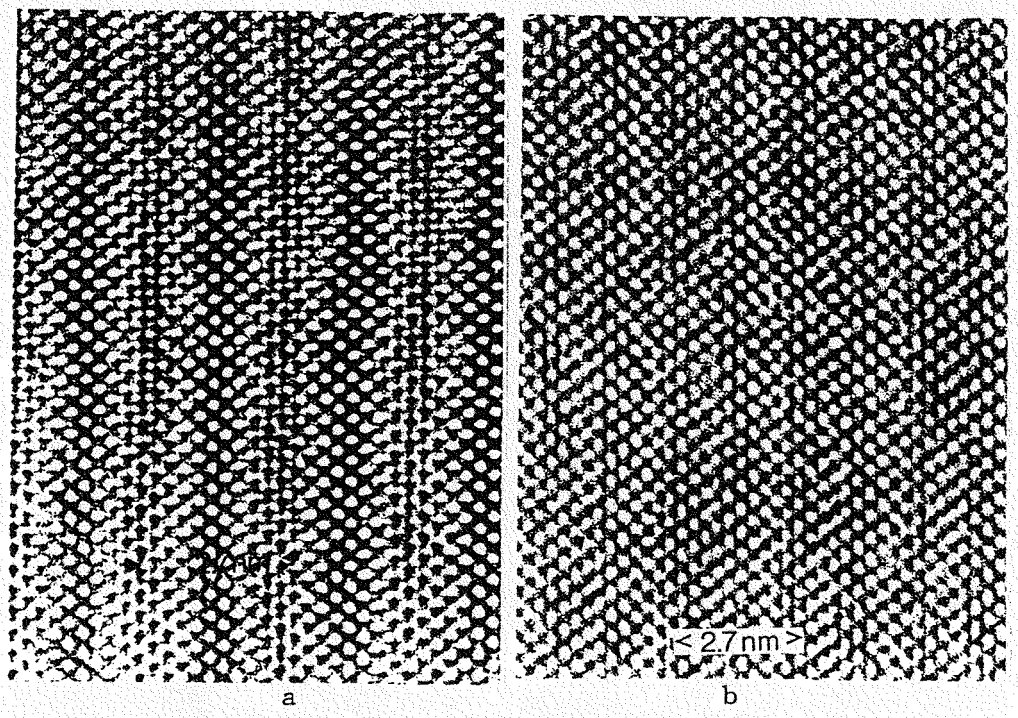

Figure 3. High resolution images [hoℓ] zone axes: a) high T_c phase; b) low T_c phase.

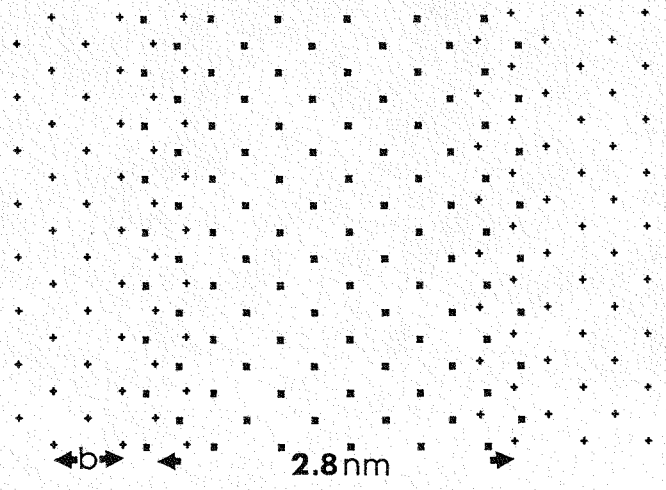

Figure 4. Drawing derived from photograph in Figure 3a.

These form a well defined lattice with uniform spacings between lattice points, but only within bands perpendicular to b. The width of the modulation vector is approximately five times b. Adjacent bands show similar lattices, with displacements relative to one another like those in antiphase domains, but with smaller displacement vectors. These vary from domain to domain. This is demonstrated in the drawing in Figure 4, which has been derived from the high resolution image in Figure 3a. The domains overlap within 5 to 10 Å regions with diminishing intensities towards the boundaries of the regions.

The main displacement is along b, but the exact direction of a component perpendicular to b has yet to be determined. It should be noticed that b is not exactly parallel to the modulation vector.

The displacement in the low T_c phase, although present, is much less pronounced.

An attempt is under way to determine the displacement vectors more exactly and to understand the displacements in terms of ordering of atoms.

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