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Modulated structure of an 800 Å epitactic film of the superconductor $Bi_2Sr_2CaCu_2O_8$ as studied by synchrotron radiation

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Abstract. The modulated structure of an 800 Å epitactic thin film of the $Bi_2Sr_2CaCu_2O_8$ superconductor has been determined using synchrotron radiation. The study shows that single-crystal techniques can be applied to very thin oriented films.

Introduction. The availability of high-intensity synchrotron sources has led to the development of the field of 'microcrystallography' using very small amounts of scattering matter (Rieck, Euler, Schulz & Schildkamp, 1988; Harding, 1990). It is of interest to investigate to what extent such studies can be extended to the bulk structure of epitactic thin films, which are often prepared in materials-science studies, and used in practical applications. Marsh, Fleming, Mandich, DeSantolo, Kwo, Hong & Martinez-Miranda (1988) have determined the structure of a 6000 (500) Å thin film of the superconductor $YBa_2Cu_4O_8$, using 39 reflections collected with a rotating-anode generator. Synchrotron radiation is likely to lower further the limit of films of which the detailed structure can be determined. We describe here such a study of an 800 Å average thickness film (with a maximum deviation estimated at 200 Å) of the $Bi_2Sr_2CaCu_2O_8$ superconductor.

Experimental. The film was grown by depositing a drop of liquid ethyl hexanoate precursor $[M(OOC_8H_{15})_x]$ in chloroform consisting of a mixture of the four hexanoate salts, with cation ratio Bi:Sr:Ca:Cu = 2.2:1.5:0.9:2, on a (100) single-crystal $LaAlO_3$ substrate mounted on a photoresist spinner. The spinner was rotated at 7000 rev min^{-1} for 10 s. The coated crystal was placed into a furnace at 673 K in air for 30 s to remove the organic precursor. The superconducting two CuO_2-layer phase was then formed by heating the sample rapidly to 1083 K. After a period of 30 min the film was air-quenched to room temperature. Energy-dispersive X-ray analysis (EDX), with correction using binary compound standards, shows the composition to be $Bi_{2.15}Sr_{1.55}Ca_{0.92}Cu_2O_{8+y}$, *i.e.* essentially identical to the starting composition. The T_c (zero-resistance) value of the sample was found to be 80 K, with a critical current density of the order of 10^4 A cm^{-2} at 70 K.

Measurements were made on the SUNY X3 beamline at the National Synchrotron Light Source at Brookhaven National Laboratory. The sample was mounted on a Huber four-circle diffractometer, with its normal within 0.5° of the ϕ axis of the diffractometer. This orientation gives identical angles between the normal to the sample and the incident and diffracted beams, which facilitates the absorption correction.

The *c*-axis-oriented sample (*i.e.* **c** perpendicular to the surface) showed two major domains related by a 90° rotation around the *c* axis. This leads to overlap of the main reflections, but not of the satellites, which are displaced along the *a* axis from the main reflections. Determination of the twin ratio can therefore be based on the measurement of pairs of satellite reflections. Data were collected with a beam of wavelength 1.4 Å, and a cross section of 0.5 × 0.6 mm. The small beam size ensures that, even at low values of the angle of incidence, the whole beam is intercepted by the sample. The volume of scattering matter in the beam is about 24 × 10^3 μm^3, or equivalent

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Table 1. *Crystal data*

	Thin film	Single crystal
a (Å)	5.420(1)	5.408(1)
b (Å)	5.409(2)	5.413(1)
c (Å)	30.76(1)	30.871(5)
Space group	*M*:*A*2*aa*:Ī11	*M*:*A*2*aa*:Ī11
Z	4	4
No. of reflections [$I > 3\sigma(I)$]	419	658
Main	187	409
1st satellite	183	188
2nd satellite	49	61
No. of variables	117	116
R/*wR* (all)*	0.117/0.131	0.072/0.074
R/*wR* (main)	0.136/0.148	0.070/0.073
R/*wR* (1st satellite)	0.090/0.115	0.065/0.068
R/*wR* (2nd satellite)	0.099/0.114	0.161/0.145

*$w = 1/\sigma^2$ with $\sigma(F^2) = [(0.02\ F^2)^2 + \sigma^2_{stat}]^{1/2}$ and $\sigma(F) = [1/(2F)]\sigma(F^2)$.

Table 2. *Positional parameters of the average structure*

The first row gives the single-crystal results; the second row gives the results of this work.

	x	y	z
Bi	0.505(2)	0.2327(5)	0.0523(1)
	0.497(4)	0.2323(7)	0.0524(1)
Sr	0.0	0.2525(5)	0.1408(1)
	0.0	0.2516(8)	0.1408(3)
Cu	0.5	0.2499(6)	0.1965(1)
	0.5	0.249(1)	0.1973(4)
Ca	0.0	0.25	0.25
	0.0	0.25	0.25
O(1)	0.75	0.0	0.197(1)
	0.75	0.0	0.198(1)
O(2)	0.25	0.5	0.199(1)
	0.25	0.5	0.201(1)
O(3)	0.53(2)	0.289(6)	0.116(1)
	0.52(1)	0.304(9)	0.109(2)
O(4)	0.02(2)	0.157(5)	0.056(2)
	-0.02(2)	0.196(9)	0.057(2)

Table 3. *Thermal parameters* (Å^2 × 10^3)

The first row gives the single-crystal results; the second row gives the results of this work. The temperature factor is defined as $\exp[-2\pi^2(U_{11}h^2a^{*2} + ... + 2U_{23}klb^*c^*)]$.

	U_{11}/U_{iso}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Bi	71(3)	21(2)	13(2)	-8(4)	10(4)	-4(2)
	102(6)	50(4)	60(3)	-18(6)	7(6)	0(2)
Sr	23(2)	5(2)	21(2)	0	0	5(3)
	42(6)	35(5)	84(6)	0	0	3(3)
Cu	10(2)	-1(3)	23(3)	0	0	-4(4)
	4(7)	28(8)	82(9)	0	0	3(4)
Ca	9(3)	5(3)	21(5)	0	0	-2(7)
	57(11)	23(9)	76(10)	0	0	5(5)
O(1,2,3,4)	10†					
	10					

† Oxygen thermal parameters not refined.

to a cube-shaped volume of 29 μm edge. The intensity of the reflections measured indicates that the experiment is not intensity limited. The considerable mosaic spread of the sample (typically 1° width) masks any diffraction spot broadening in the **c*** direction. However, significant broadening may be expected when even thinner films are used.

Reflections with angle of incidence less than 5° were rejected, as were 18 reflections which overlapped with substrate diffraction peaks. A total of 570 main and satellite intensities were recorded by a 2° step scan of the ω angle, of which 419 had $I > 3\sigma(I)$ (Table 1). 108 satellite reflections [with $I > 20\sigma(I)$] of each of the two domains were used to determine the twin ratio to be 4.5:1. The single-domain intensities of the main reflections were derived with the expression

$$I_{corr,hkl} = [R/(R-1)]I_{m,hkl} - [1/(R-1)]I_{m,khl},$$

where $I_{corr,hkl}$ is the single-domain intensity of the *hkl* reflection, I_m are the measured intensities and R is the ratio of occurrences of the main and minor domains. The satellite reflections are measured from a single domain and are scaled to the main reflections by multiplication with the factor $(R + 1)/R$.

Data were reduced by a synchrotron-specific modification of data-collection programs by Blessing (1987). Absorption corrections were performed using the appropriate expression for a thin-film sample [$(I/I_o) = (\sin\theta\sin\chi/2\mu T)[1 - \exp(-2\mu T/\sin\theta\sin\chi)]$, where T is the film thickness and μ is the linear absorption coefficient]. The program *JANA* was used in the analysis of the structural modulation (Petříček & Coppens, 1988). The model for the modulation was identical to that used in the single-crystal analysis, and included the oxygen modulation (Petříček, Gao, Lee & Coppens, 1990). The Sr occupancy was kept fixed at the EDX values, while the Bi occupancies of the Bi, Sr and Ca sites were refined to values of 0.95(3), 0.10(2) and 0.13(2) respectively. For the Ca site the constraint Ca + Bi = 1.0 was used. The occupancies of the Cu sites were fixed at one. The corresponding composition is $Bi_{2.23}Sr_{1.55}Ca_{0.87}Cu_2O_8$, which agrees within the experimental uncertainties with the EDX values. The partial occupancy of the Sr and Ca sites by Bi atoms is in agreement with previous single-crystal studies using the anomalous-scattering technique (Coppens, Lee, Gao & Sheu, 1991). Agreement factors obtained (Table 1) are comparable with those from the single-crystal analysis. Positional parameters of the average structure are identical within the experimental accuracy to those for the single crystal, with the possible exception of the y coordinate of O(4) (Table 2). The average thermal parameters are, however, considerably higher than the single-crystal results, in particular in the c-axis direction (Table 3), possibly indicating less than perfect order in the approximately 25 unit-cell-thick film.

Discussion. The amplitudes of the positional modulation are very close to those in the single crystal, except for the modulation of O(4), the oxygen atom in the Bi plane, which appears somewhat smaller. The displacements of this atom are properly described by a linear rather than sinusoidal modulation function (Petříček, Gao, Lee & Coppens, 1990). Given the weakness of the oxygen scattering, the information on the oxygen modulation is less reliable

Table 4. *Amplitudes* (Å) *of the positional modulation of the heavy atoms*

The first row gives the single-crystal results; the second row gives the results of this work.

	WAVE	U_x	U_y	U_z
Bi	$\sin(2\pi x_4)$	0.33(1)	0.06(1)	−0.01(1)
		0.341(7)	0.01(1)	−0.03(2)
	$\cos(2\pi x_4)$	0.08(2)	−0.04(1)	−0.16(1)
		0.02(3)	−0.05(1)	−0.152(6)
	$\sin(4\pi x_4)$	0.09(1)	0.01(2)	−0.06(1)
		0.03(1)	0.04(3)	−0.04(1)
	$\cos(4\pi x_4)$	−0.01(2)	−0.11(1)	−0.06(1)
		0.01(2)	0.05(2)	−0.03(1)
Sr	$\sin(2\pi x_4)$	0.22(1)	0.0	0.0
		0.25(1)	0.0	0.0
	$\cos(2\pi x_4)$	0.0	0.04(3)	−0.21(1)
		0.0	0.02(1)	−0.22(1)
	$\sin(4\pi x_4)$	0.10(1)	0.0	0.0
		0.10(2)	0.0	0.0
	$\cos(4\pi x_4)$	0.0	0.02(4)	−0.07(2)
		0.0	−0.01(4)	−0.04(2)
Ca	$\sin(2\pi x_4)$	0.0	0.0	0.0
		0.0	0.0	0.0
	$\cos(2\pi x_4)$	0.0	−0.01(5)	−0.26(1)
		0.0	0.03(2)	−0.27(2)
	$\sin(4\pi x_4)$	−0.04(2)	0.0	0.0
		−0.01(3)	0.0	0.0
	$\cos(4\pi x_4)$	0.0	0.0	0.0
		0.0	0.0	0.0
Cu	$\sin(2\pi x_4)$	0.06(1)	0.0	0.0
		0.06(1)	0.0	0.0
	$\cos(2\pi x_4)$	0.0	−0.03(2)	−0.21(1)
		0.0	−0.01(2)	−0.28(2)
	$\sin(4\pi x_4)$	−0.01(1)	0.0	0.0
		0.00(2)	0.0	0.0
	$\cos(4\pi x_4)$	0.0	0.08(3)	−0.07(1)
		0.0	−0.01(7)	−0.02(2)

than that of the heavier atoms, which is given in Table 4. The modulation of the bismuth thermal parameter is essentially the same as that found in the single crystal.

The results establish that the structural modulation of this '2212' BiSrCaCuO thin film is very similar to that of the single crystal, and that it can be present in samples with reasonably high values of J_c and T_c.

Variations in the composition (Golden, Bloomer, Lange, Segadaes, Vaidya & Cheetham, 1991) and detailed structure of the superconducting phases (Gao, Lee, Coppens, Subramanian & Sleight, 1988; Lee, Gao, Sheu, Petříček, Restori, Coppens, Darovskikh, Phillips, Sleight & Subramanian, 1989; Gao, Lee, Ye, Bush, Petříček & Coppens, 1989; Gao, Lee, Graafsma, Ye, Bush, Petříček & Coppens, 1990) make it desirable that the different measurements be performed on identical samples. This permits a direct correlation between properties, structure and composition. The thin-film diffraction technique is well suited for such studies.

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