X-ray determination of mosaic structure in variable thickness EuBa$_2$Cu$_3$O$_{7-\delta}$ thin films

S C Wimbush$^{1,3}$, M C Li$^{1,4}$, M E Vickers$^1$, Q X Jia$^2$ and J L MacManus-Driscoll$^1$

$^1$ Department of Materials Science and Metallurgy, University of Cambridge, Pembroke Street, Cambridge CB2 3QZ, UK
$^2$ Superconductivity Technology Center, MS K763, Los Alamos National Laboratory, Los Alamos, NM 87545, USA

Abstract. Employing the Srikant method of extrapolating the rocking curve widths of a series of diffraction peaks across a range of angles of inclination, the out-of-plane (mosaic tilt) and in-plane (mosaic twist) misorientation angles of a series of varying thickness EuBa$_2$Cu$_3$O$_{7-\delta}$ thin films has been deduced. The twist angle is seen to increase as the film thickness decreases below 200 nm, from 0.2° for films approaching the bulk to 0.35° for the thinnest film (50 nm) investigated. The tilt angle follows a similar trend, increasing more strongly from 0.05° to 0.4°. Furthermore, it is shown that the tilt and twist misorientations in this class of materials are independent in nature, implying that limited information regarding the in-plane behaviour can be inferred from purely out-of-plane measurements. The reduction in the degree of misorientation in thicker films can be associated with a decreasing threading dislocation density, and correlates with the decrease in the critical current density of R123 thin films with increasing film thickness.

1. Introduction
Thin films of the promising family of high-temperature rare earth superconductors RBa$_2$Cu$_3$O$_{7-\delta}$ (R123, where R is any rare earth) typically exhibit a reduction in critical current density, $J_c$, with increasing film thickness [1], acting as a limitation on their widespread practical application. A full explanation of this behaviour, hoped to provide a means of overcoming it, is yet elusive.

Of critical importance to the issue of $J_c$ enhancement is the existence of defects within the film that provide pinning sites to hinder the dissipative motion of magnetic flux lines. One such naturally occurring defect is the dislocation network that accommodates the mosaic structure of epitaxial thin films. Such dislocations have in the past been imaged via scanning tunnelling microscopy [2], which is sensitive only to screw dislocations, and by etching and atomic force microscopy visualisation [3], which while sensitive to all dislocations, is also destructive. Both of these methods suffer from the drawbacks of being selective and surface sensitive.

In this contribution, we have used x-ray diffraction techniques to examine the microstructural properties of a series of thin film samples of EuBa$_2$Cu$_3$O$_{7-\delta}$ of varying thickness with the aim of elucidating the essential difference in the crystallography of the thinner samples that might lead to the observed $J_c$ enhancement.

$^{3}$ To whom any correspondence should be addressed. E-mail: scw42@cam.ac.uk.
$^{4}$ Current address: School of Materials Science and Engineering, Harbin Institute of Technology, P O Box 405, 92 West Da-Zhi Street, Nangang District, Harbin 150001, China.
2. Experimental

Thin films of EuBa$_2$Cu$_{3.7}$O$_{7-δ}$ grown epitaxially on SrTiO$_3$ single crystal substrates by pulsed laser deposition using a YBa$_2$Cu$_{3.7}$O$_{7-δ}$ seed layer [4] were studied using x-ray diffraction. Four samples of thicknesses 50 (estimated), 150, 200 and 330 nm were investigated. The inductively-measured superconducting transition temperatures, $T_c$, of the samples were all 93 K, with transition widths of around 0.5 K.

On each sample, rocking curves ($\omega$-scans) of a range of peaks chosen to span as much of the inclination range from out-of-plane ([001] direction, $\psi = 0^\circ$) to in-plane ($\psi = 90^\circ$) as could be accessed were measured in asymmetric diffraction geometry on a Philips X'Pert MRD. An x-ray mirror provided a parallel beam geometry, making the setup impervious to defocusing effects as the sample was tilted through a wide range of $\omega$ angles. To achieve sufficient intensity to measure these high-order peaks on samples as thin as 50 nm, the instrument was operated in a medium resolution mode using $\frac{\lambda}{8}$ divergence and anti-scatter slits, and a 0.35 mm wide receiving slit. Soller slits were omitted for a further intensity gain, enabling an adequate rocking curve measurement to be completed in around 30 minutes, at 10 s measurement time per data point. In such a setup, however, the instrumental broadening of the peaks is quite significant, as can be seen on the example rocking curves shown in figure 1 for the strongest peaks of both the thickest sample and a Si wafer, and must be carefully accounted for. This was done by measuring a full set of peaks of the Si wafer, and attributing their breadth entirely to instrumental broadening. A simple empirical fit to the data, shown in figure 2, was then used to interpolate this breadth to any 2θ position, and the resultant values subtracted from the measured peak widths to correct for the instrumental broadening component.

![Figure 1. Example rocking curves of the thickest sample (+) and a Si wafer (×). Solid lines are fits to the curves, with difference plots shown at the bottom of the graph.](image1)

![Figure 2. Peak widths of a Si wafer, used to determine the instrumental broadening. Solid line fits to the data and the equations shown are empirical.](image2)

In addition to the instrumental broadening, a significant contribution due to size broadening arises, particularly in the thinnest film investigated, and must also be corrected for. This was done by taking the film thickness as the critical domain size in the out-of-plane direction and scaling it appropriately with the inclination angle, where the in-plane domain (grain) size is supposed large enough not to contribute to any peak broadening.

Rocking curves were generally fit using a pseudo-Voigt function, although the curves measured on Si were well fit with a pure Gaussian lineshape. The pseudo-Voigt peak function is a simple approximation to the convolution of Gaussian and Lorentzian functions formed from a weighted sum of the two, and is fully defined by its baseline $I_0$, centre position $\omega_0$, the peak area (here, the integral intensity) $A$, the peak width, here expressed as an integral breadth $\beta$, and the Lorentzian fraction $\mu$:

$$I(\omega) = I_0 + A \left[ \mu \left( \frac{\sigma^2}{\beta}(\omega - \omega_0)^2 + \beta \right)^{-1} + (1 - \mu) \frac{1}{\beta} e^{-\frac{(\omega - \omega_0)^2}{\beta^2}} \right]$$

(1)
A model, described by Srikant et al. [5] for the evaluation of mosaic structure in epitaxial thin films was applied to the rocking curve data to enable extrapolation along the angle of inclination, $\psi$, to pure out-of-plane ($\psi = 0^\circ$) and in-plane ($\psi = 90^\circ$) values. The Srikant analysis consists in performing a numerical convolution of the two peak shapes that result from the out-of-plane mosaic tilt and in-plane mosaic twist components of the peak broadening, $\beta_{\text{tilt}}$ and $\beta_{\text{twist}}$, at a given angle of inclination, $\psi$. From the rotation of a rigid body:

$$\beta_{\text{tilt}}^0(\psi) = \cos^{-1}[\cos^2(\psi) \cos(\beta_{\text{tilt}}) + \sin^2(\psi)]$$  
(2a)

$$\beta_{\text{twist}}^0(\psi) = \cos^{-1}[\sin^2(\psi) \cos(\beta_{\text{twist}}) + \cos^2(\psi)]$$  
(2b)

Allowing for a degree of interdependence between tilt and twist, quantified by a parameter $m$, with the interaction supposed to be exponential, the above expressions are modified to read:

$$\beta_{\text{tilt}}^{\text{eff}}(\psi) = \beta_{\text{tilt}}^0(\psi) \exp\left(-m \frac{\beta_{\text{twist}}^0(\psi)}{\beta_{\text{twist}}}ight)$$  
(3a)

$$\beta_{\text{twist}}^{\text{eff}}(\psi) = \beta_{\text{twist}}^0(\psi) \exp\left(-m \frac{\beta_{\text{tilt}}^0(\psi)}{\beta_{\text{tilt}}}ight)$$  
(3b)

These can be trivially seen to reduce to the original pair of equations in the case $m = 0$. To convolute these two, Srikant derives a numerical process that yields:

$$\beta(\psi) = \left\{\left[\beta_{\text{tilt}}^{\text{eff}}(\psi)\right]^{n} + \left[\beta_{\text{twist}}^{\text{eff}}(\psi)\right]^{n}\right\}^{1/n} \quad \text{with} \quad n = 1 + (1 - \mu)^2$$  
(4)

Thus, by calculating $n$ from the Lorentzian fraction of the rocking curves, we can fit the $\beta(\psi)$ data to obtain the misorientation angles $\beta_{\text{tilt}}$ and $\beta_{\text{twist}}$.

3. Results

Table 1 summarises the results of performing pseudo-Voigt fits to each of the rocking curve measurements on each of the samples. In each case, the resultant integral breadth, $\beta$, has been corrected for instrumental and size broadening as described above. As can be seen, several of the peaks yield non-physical values of the Lorentzian fraction $\mu$. These peaks were also found to be outliers. For this reason, they have been excluded from the further analysis. The origin of these aberrant results has not yet been established, but may simply be an inadequate setup of the instrument prior to performing the respective peak measurement.

Following Srikant, we take as $\mu$ the average of all the values obtained from the rocking curve fits for a given sample. It will be noted that the values of $\mu$ obtained for different diffraction peaks of the same sample are highly variable, and thus that the average value can hardly be described as particularly representative of the sample as a whole. Fortuitously, however, the results obtained are found to depend only weakly on the exact value of $\mu$ (between 0 and 1). The Srikant fits to the rocking curve data are shown in figure 3, and the resultant fit parameters are summarised in table 2. It is seen that for all four samples, the error in the interdependence parameter $m$ coupling tilt and twist is greater than the value obtained from the fit. From this, we conclude that the two are independent. Although an additional fit parameter inevitably results in a better fit to the data, we are unable to justify the use of the interdependence parameter in this case, and so the fit was redone, holding $m$ fixed at zero. The results of this fit were those used to obtain the tilt and twist angles, although both fits are shown on figure 3 for comparison. The curves are seen to track each other closely, and the different tilt and twist values to lie within the margin of error of the fit.
Table 1. Parameters of pseudo-Voigt fits to rocking curves of EuBa$_2$Cu$_3$O$_{7-δ}$ samples of different thicknesses. The error in the last digit resulting from the peak fitting process is indicated in parentheses. Peaks excluded from subsequent analysis are highlighted in grey.

|        | 50 nm   | 150 nm  | 200 nm  | 330 nm  |
|--------|---------|---------|---------|---------|
| $\psi$ | $\beta$ | $\mu$   | $\beta$ | $\mu$   | $\beta$ | $\mu$   |
| (1113) | 18.2    | 0.423(6)| 0.59(3) | 0.213(6)| 0.61(3) | 0.130(5)| 0.30(2) | 0.096(7)| 0.50(1) |
| (1110) | 23.2    | 0.408(5)| 0.51(3) | 0.208(4)| 0.37(3) | 0.143(4)| 0.33(2) | 0.108(5)| 0.41(2) |
| (1213) | 27.4    | 0.448(7)| 0.19(5) | 0.718(14)| 1.86(4) | 0.244(15)| 1.20(8) | 0.143(10)| 0.90(7) |
| (2113) | 27.6    | 0.491(11)| 0.41(6) | 0.220(6)| 0.28(4) | 0.199(10)| 0.99(6) | 0.127(7)| 0.55(2) |
| (0210) | 31.0    | 0.589(8)| -1.86(7)| 0.257(6)| 0.52(4) | 0.176(5)| 0.63(2) | 0.146(5)| 0.49(3) |
| (2010) | 31.3    | 0.578(11)| -0.82(9)| 0.232(5)| 0.40(3) | 0.168(4)| 0.38(2) | 0.138(5)| 0.45(2) |
| (1210) | 34.0    | 0.468(4)| 0.22(2) | 0.365(4)| -0.25(3)| 0.191(6)| 0.78(4) | 0.153(7)| 0.85(4) |
| (2110) | 34.2    | 0.481(6)| 0.13(4) | 0.232(4)| 0.39(2) | 0.175(4)| 0.53(2) | 0.138(4)| 0.48(2) |
| (0310) | 42.0    | 0.408(6)| 0.55(3) | 0.230(4)| 0.43(2) | 0.161(5)| 0.49(2) | 0.173(10)| 0.94(6) |
| (3010) | 42.4    | 0.489(20)| 0.78(9) | 0.243(7)| 0.58(4) | 0.166(5)| 0.56(2) | 0.149(5)| 0.58(2) |
| (238)  | 53.7    | 0.430(7)| 0.61(3) | 0.276(5)| 0.63(3) | 0.252(5)| 0.53(3) | 0.171(5)| 0.62(2) |
| (328)  | 53.8    | 0.442(10)| 0.59(5) | 0.329(8)| 0.69(4) | 0.237(6)| 0.74(4) | 0.203(6)| 0.68(4) |
| (147)  | 60.6    | 0.373(11)| 0.68(5) | 0.245(6)| 0.50(3) | 0.217(5)| 0.40(3) | 0.200(6)| 0.43(3) |
| (417)  | 60.8    | 0.379(14)| 0.60(8) | 0.246(6)| 0.57(3) | 0.187(5)| 0.58(2) | 0.171(5)| 0.53(2) |
| (245)  | 69.6    | 0.392(6)| 0.63(3) | 0.282(5)| 0.41(3) | 0.247(5)| 0.18(3) | 0.235(5)| 0.07(4) |
| (425)  | 69.8    | 0.410(8)| 0.69(4) | 0.313(6)| 0.54(3) | 0.246(5)| 0.42(3) | 0.213(5)| 0.37(3) |

Figure 3. Srikant analysis of the rocking curve widths of EuBa$_2$Cu$_3$O$_{7-δ}$ films of thickness (a) 50 nm, (b) 150 nm, (c) 200 nm and (d) 330 nm, corrected for instrumental and size broadening. Solid curves are fits to the data assuming that tilt and twist are independent ($m = 0$); broken curves are fits allowing for a degree of interdependence as described in the text.
Table 2. Resultant fit parameters from Srikant fits.

| Thickness | μ_{average} | m | \( \beta_{tilt} \) (°) | \( \beta_{twist} \) (°) |
|-----------|-------------|---|------------------------|------------------------|
| 50 nm     | 0.33 ± 0.19 | -0.18 ± 0.23 | 0.43(2)                | 0.34(2)                |
| 150 nm    | 0.50 ± 0.12 | 0.24 ± 0.31  | 0.15(2)                | 0.27(2)                |
| 200 nm    | 0.52 ± 0.21 | 0.24 ± 0.37  | 0.09(2)                | 0.23(2)                |
| 330 nm    | 0.55 ± 0.22 | 0.23 ± 0.26  | 0.05(1)                | 0.22(1)                |

In figure 4, we plot the variation in the tilt and twist angles with film thickness. The twist angle is seen to level off and remain rather constant at around 0.2° for films thicker than about 200 nm, while increasing as the thickness drops below 200 nm, to reach about 0.35° at 50 nm thickness. The tilt angle is seen to be around 0.4° in the thinnest film, but drops off more rapidly as the thickness increases, reducing to around 0.05° in the thickest film studied. This mosaicity may be linked to the density of threading dislocations geometrically required to produce the observed lattice distortion, with screw threading dislocations generating the mosaic tilt, and edge threading dislocations the mosaic twist [6], as illustrated in figure 5. Here, we apply the simple equation mentioned in [7] to obtain a rough estimate of these dislocation densities, although more rigorous (and involved) models have been proposed [8]. From the variation in tilt angle, we obtain screw dislocation densities (for Burgers vector \( b = [001] \)) ranging from \( 1 \times 10^7 \) cm\(^{-2} \) for the thickest film to \( 9 \times 10^6 \) cm\(^{-2} \) for the thinnest, and from the variation in twist angle, we obtain edge dislocation densities (for \( b = [100] \)) ranging from \( 2 \times 10^6 \) cm\(^{-2} \) to \( 5 \times 10^5 \) cm\(^{-2} \). The range of screw dislocation densities is thus comparable with that reported in [2] for films having critical current densities of the order of \( 5 \times 10^7 \) A cm\(^{-2} \) at 4.2 K, while the overall dislocation density, dominated by the edge dislocations, is in the same range as that reported in [3] for films with critical current densities ranging from \( 10^6 \) to \( 10^8 \) A cm\(^{-2} \) at 4.2 K.

4. Conclusions
A careful analysis of a large number of accessible diffraction peaks in thin films of EuBa\(_2\)Cu\(_3\)O\(_{7-\delta}\) of varying thickness has enabled the out-of-plane mosaic tilt and in-plane mosaic twist of the samples to be determined. The two have been shown to be primarily independent of each other. Both aspects of the mosaicity are seen to increase in the thinner films, leveling off for films thicker than around 200 nm. The mosaic tilt determined via this technique is seen to drop off more rapidly than the mosaic twist, with both becoming comparable in the thinnest film studied. An estimate of the threading dislocation densities required to generate these degrees of misorientation gives values of \( 10^7 \) to \( 10^{10} \) cm\(^{-2} \), corresponding to the sort of dislocation densities reported via direct observation. The reduction in dislocation density in thicker films may go some way towards explaining the commonly observed decay in critical current density with film thickness.
Acknowledgments
This work is supported by the UK Engineering and Physical Sciences Research Council as part of the project, “Novel materials nano-engineering for enhanced performance of superconductor coated conductors and functional oxides”.

References
[1] Foltyn S R, Wang H, Civale L, Jia Q X, Arendt P N, Maiorov B, Li Y, Maley M P and MacManus-Driscoll J L, 2005 Appl. Phys. Lett. 87 162505
[2] Mannhart J, Anselmetti D, Bednorz J G, Catana A, Gerber Ch, Müller K A and Schlom D G, 1992 Z. Phys. B 86 177
[3] Dam B, Huijbregtse J M, Klaassen F C, van der Geest R C F, Doornbos G, Rector J H, Testa A M, Freisem S, Martinez J C, Stäuble-Pumpin B and Griessen R et al., 1999 Nature 399 439
[4] Jia Q X, Foltyn S R, Arendt P N, Wang H, MacManus-Driscoll J L, Coulter Y, Li Y, Maley M P and Hawley M, 2003 Appl. Phys. Lett. 83 1388
[5] Srikant V, Speck J S and Clarke D R, 1997 J. Appl. Phys. 82 4286
[6] Heying B, Wu X H, Keller S, Li Y, Kapolnek D, Keller B P, DenBaars S P and Speck J S, 1996 Appl. Phys. Lett. 68 643
[7] Metzger T, Höpler R, Born E, Ambacher O, Stutzmann M, Stömmer R, Schuster M, Göbel H, Christiansen S, Albrecht M and Strunk H P, 1998 Phil. Mag. A 77 1013
[8] Kaganer V M, Kohler R, Schmidbauer M, Opitz R and Jenichen B, 1997 Phys. Rev. B 55 1793