An aging effect and its origin in GdBCO thin films

K Schlesier\textsuperscript{1,2}, H Huhtinen\textsuperscript{1}, S Granroth\textsuperscript{3} and P Paturi\textsuperscript{1}

\textsuperscript{1} Wihuri Physical Laboratory, Department of Physics and Astronomy, FI-20014 University of Turku, Finland
\textsuperscript{2} Graduate School of Materials Research, Turku, Finland
\textsuperscript{3} Materials Research Laboratory, Department of Physics and Astronomy, FI-20014 University of Turku, Finland

E-mail: kim.schlesier@utu.fi

Abstract. An aging effect investigation was made for GdBa$_2$Cu$_3$O$_7$ (GdBCO) thin films grown on SrTiO$_3$ (001) substrates with pulsed laser deposition (PLD) method from nanograined targets. The films were cut into two pieces where one piece was coated with gold cap layer while the other was left without coating. Both pieces were kept in ambient air during the half year measurement period. Magnetization measurements as well as phase purity, lattice parameter, oxygen effect and depth structure determination with x-ray diffraction (XRD) were made in one month interval. For structure and oxygen content, x-ray photoelectron spectroscopy measurements (XPS) were done in the beginning and in the end of the period. A reduction of the critical temperature and the critical current density, $J_c$, was found in the gold coated GdBCO film in ambient air in course of time. A smaller decrease of $J_c$ was detected in uncoated GdBCO. No development of impurity phase, increase of a–orientation or reduction of the pinning structure was detected in uncoated GdBCO. However, a small development of impurity phase was found in gold coated GdBCO. The diminution of $T_c$ and $J_c$ is concluded to originate from oxygen release. No such a phenomenon was found in YBa$_2$Cu$_3$O$_7$. We conclude that gold is not a proper cap layer at least for some applications.

1. Introduction

YBa$_2$Cu$_3$O$_{7-\delta}$ (YBCO) is one of the most promising high temperature superconductor (HTS) materials because of its high irreversibility field, $B_{\text{irr}}$, and critical temperature, $T_c$. The $T_c$ can be enhanced by substituting Y with Gd. That is why GdBa$_2$Cu$_3$O$_{7-\delta}$ (GdBCO) has higher $B_{\text{irr}}$ and critical current density, $J_c$, at 77 K [1, 2, 3]. GdBCO is also more isotropic [2, 4, 5, 6, 7]. Although modern techniques allow growth of thick YBCO films without significant increase of a–orientated grains, the volume of a–oriented grains does not increase as much with increasing film thickness as in YBCO in a standard growth process, which results in better critical current, $I_c$, in thick films [6, 8]. Moreover, GdBCO can be grown at lower substrate temperatures than YBCO and it can be also ablated in-plume in pulsed laser deposition method (PLD) [9] leading to lower production costs and higher production yield. Indeed, its potential has been illustrated by fabricating long coated conductors [5, 10] and a test coil [11, 12].

The $J_c$ in GdBCO compared to YBCO in high field and more isotropic $J_c$ [2] might arise from extra stacking faults [2, 4, 13]. These stacking faults are formed by growth of extra Gd layer which forms an edge dislocation and shifts the other layers such as Cu-O and Ba-O causing layer mismatch [13].
The $T_c$ of these copper oxide HTS materials is determined by oxygen content: for $\delta \geq 0.2$. $T_c$ drops \cite{14, 15}. Also, the reduction of the oxygen content can be seen as a change in lattice parameters $a$, $b$ and $c$ \cite{14, 15} and their values can be used to estimate the oxygen content in bulks \cite{14}, but in the case of thin films this estimation might not hold, because these parameters depend on deposition temperature, dislocation density, and substrate material too. Instead, the intensity ratios of (00$l$) reflections of YBCO in x-ray diffraction (XRD) depend only on oxygen content in thin films \cite{15}. That is why the intensity ratios of these peaks can be used as an estimate for oxygen content. We note here that this estimation might not hold for GdBCO because cation substitution is easier with Gd and Ba than with Y and Ba, since Gd has closer radius to Ba than Y.

Though GdBCO is very promising material for application, a problem might be the observed aging effect observed by Li et al., ref. \cite{16} and by us in all of those GdBCO films we have remeasured after a period of time. This aging effect is not present in YBCO as far as we know. Usually, a cap layer is used to protect the superconductor material that is probably why there are not so many indications of this phenomenon in literature. The cap layers used are for example gold \cite{9}, silver \cite{17}, Kapton with adhesive \cite{18}, SrTiO$_3$ \cite{19} etc.

In this paper, we have investigated the development of aging effect in GdBCO with time. The results in GdBCO were compared with the results of YBCO.

2. Experimental

The nanosized precursor powders were made with sol–gel-method, the details are presented elsewhere \cite{20, 21}; the increase in $J_c$ by using nanograin target in comparison to commercially available micronized target material has been reported in ref. \cite{22} and \cite{23}. The thin films were grown with PLD on SrTiO$_3$ (STO) (001) substrates, and the optimized ablation temperature, $T_s$, was 700°C and 745°C for GdBCO and YBCO films, respectively. In this study, the optimum energy densities were the same for both materials due to target aging and treatments for GdBCO, in contrast with earlier results \cite{21}. The thickness of the films was 180 nm, which was estimated from pulse number, 1 Å/pulse, which was based on our previous thickness measurements \cite{21}. The films of high quality were split and one half was gold coated (Au-YBCO and Au-GdBCO) and the other half was left without coating (uc-YBCO and uc-GdBCO) for both the films. The gold coating was made with sputtering in slightly below the room temperature in a separate chamber. The thickness of Au layer was 50 nm for YBCO and 100 nm for GdBCO to take into account the difference of the surface roughnesses. The cap layer thickness was estimated from sputtering time. All the films were kept in ambient air for the whole measurement period. The films were measured with ac- and dc-magnetization methods and $2\theta$ and rocking curve scans with x-ray diffraction (XRD) during five months with one month interval. Two other uncoated GdBCO films ablated in the optimum conditions were made for Bragg-angle–rotation-angle ($2\theta, \phi$) 2D x-ray diffraction and x-ray photoelectron spectroscopy (XPS). These two measurements were made for fresh and about 7–8 months old samples. From ac-magnetization measurements the $T_c$ was estimated from the onset of real part of ac-magnetisation. The critical current density was estimated from dc-magnetization measurements by Bean model: $J_c = 2\Delta m/\pi(a(1-a/3b)V)$, where $a$ and $b$ ($b \geq a$) are the length and the width, $V$ is the volume of the sample and $\Delta m$ is the opening of the magnetization curves \cite{24, 25, 26}.

The magnetization measurements were made with Quantum Design Physical Properties Measurements System, and XRD with X’Pert Pro diffractometer with Cu Kα radiation. The XPS spectra were obtained by Perkin-Elmer PHI 5400 spectrometer using monochromatised Mg Kα excitation (1253.6 eV). 89.45 eV analyzer pass energy and 45° take-off angle were used to measure the core-level spectra shown in this study. The base pressure in the analyzer chamber was around 2×10$^{-9}$ Torr during the measurements. The binding energy (BE) scale was calibrated using the C 1s core-level of the sample and the standard Au 4f$_{7/2}$ (BE=83.98
Table 1. The rocking curve full width at half maximum values, initial critical current densities, $J_c$, and initial critical temperatures of uncoated-YBCO (uc-YBCO), gold-coated YBCO (Au-YBCO), uncoated GdBCO (uc-GdBCO) and gold-coated GdBCO (Au-GdBCO) thin films.

|                  | uc-YBCO | Au-YBCO | uc-GdBCO | Au-GdBCO |
|------------------|---------|---------|----------|----------|
| Rocking curve (005) width ($^\circ$) | 0.25    | 0.25    | 0.20     | 0.20     |
| Initial $J_c$ at 10 K ($10^7 \cdot A/cm^2$) | 3.11    | 1.51    | 2.60     | 1.81     |
| Initial $J_c$ at 77 K ($10^6 \cdot A/cm^2$) | 2.16    | 0.85    | 3.15     | 1.83     |
| Initial $T_c$ (K) | 89.0    | 89.0    | 91.5     | 91.5     |

Figure 1. The 2$\theta$-scan of Au-GdBCO (a) and the development of the lattice parameter $c$ (b) with time.

eV) reference line.

3. Results

3.1. Structural properties
The XRD 2$\theta$-scans in (00$l$)-direction did not show any impurity peaks for uc-YBCO, Au-YBCO and uc-GdBCO at any point of measurement period. For fresh Au-GdBCO, no impurity peaks were detectable, but some minor impurity peaks appeared in the aged film (figure 1 (a)), possibly due degradation of the material or development of an impurity in the surface area resulted by the Au coating. Those impurities seem to be BaO, Ba and CuO as well as unidentified peaks was detected. The rocking curve widths, which were calculated from fitted values for Gaussian line-shapes, did not show any growth or shrinkage for any of the films. The full width at half maximum values are presented in table 1. The $c$ parameter was approximately constant (figure 1 (b)) during the measurement period for uc-YBCO, Au-YBCO and uc-GdBCO, but in contrast, Au-GdBCO showed clear increase in $c$ parameter. This means that in former case the oxygen content or number of crystal defects remained the same, but in latter case there is a decrease in oxygen content or in number of crystal defects. The XRD (2$\theta$, $\phi$)-scans for (102) peak did not show any change in the volume of $a$-oriented grains for uncoated GdBCO in 8 months. Neither did (2$\theta$, $\phi$)-scans for (212)-peak show any major change in twinning structure and dislocation density for uncoated GdBCO within 8 months. The peak intensity ratios, which can be used for oxygen content determination in YBCO [15], show (figure 2) no change in oxygen content in uc-YBCO and Au-YBCO. In contrast the intensity ratios show clear change in oxygen content for uc-GdBCO and Au-GdBCO during the first month and minor or no change in later measurements. The $I(005)/I(004)$-ratio indicates about 0–0.2 of change of $\delta$ in uc-GdBCO
Figure 2. The time dependence of (a) $I(005)/I(004)$-ratio and (b) $I(005)/I(007)$-ratio.

Figure 3. The real part of ac-magnetization $M'$ and its time dependence in uc-YBCO (a), Au-YBCO (b), uc-GdBCO (c) and Au-GdBCO (d).

and some higher oxygen change in Au-GdBCO. However, the $I(005)/I(007)$-ratio indicates an abrupt (from seven to six) change in oxygen content between fresh and aged film measurements. This means that this estimation might not be completely valid for GdBCO as it is for YBCO, but these results clearly indicate a reduction of oxygen content.

3.2. Magnetic properties
The initial onset $T_c$’s are shown in table 1. There is a clear broadening in superconductivity transitions between Au- sputtered and non-sputtered films, which is probably due to development of a secondary phase with lower $T_c$ (figure 3). Sputtering seems to have an effect on $J_c$ too, as can be seen in figure 4 and table 1. Therefore Au-sputtering clearly influences superconducting properties of both the materials. This is discussed in more detail in discussion
The $J_c$ measurements of the fresh and the aged uc-YBCO (a), Au-YBCO (b), uc-GdBCO (c) and Au-GdBCO (d) thin films.

Figure 4. The $J_c$ measurements of the fresh and the aged uc-YBCO (a), Au-YBCO (b), uc-GdBCO (c) and Au-GdBCO (d) thin films.

section. The $J_c$'s of YBCO was better than GdBCO at 10 K, and at 77 K it is opposite (table 1). This might be result of higher $T_c$ of GdBCO (table 1).

A clear aging effect can be seen in $T_c$ of Au-GdBCO (figure 3 (d)) with time: fresh: 91.5 K, after one: 88.3 K, two: 86 K, three: 78.5 K, four: 73.5 K and five months: 66.5 K. Also, the width of the transition, from 90% to 10% value of $M'$, broadens, from 3.3 K to 14.6 K, in Au-GdBCO with time. No reduction of $T_c$ nor transition broadening was seen for rest of the films. A similar reduction of $J_c$ with time can be seen occurring slowly in uc-GdBCO (figure 4 (c)) for the first two months and some small changes can be seen for the rest three months. This indicates that the aging effect is rather fast in the beginning but saturates later and there is probably some interaction with air similar to the small variation which can be seen in uc-YBCO (figure 4 (a); the abrupt decrease between measurements of two and three months old sample is probably due to an appeared split or scratch on the film. The reduction of $J_c$ is fast, from 18.1 MA/cm$^2$ to 1.01 MA/cm$^2$, in Au-GdBCO at 10 K in five months (figure 4 (d)). No clear change was seen in low magnetic field plateau of $J_c$ nor in curve shape at high magnetic fields for all the films. Hence, the pinning structure did not change with time. The 77 K $J_c$ data are not presented but they are similar to 10 K data.

3.3. X-ray photoelectron spectroscopy (XPS)
XPS was used to investigate the possible changes in the oxidation state of Cu in fresh and aged uncoated GdBCO samples. The XPS spectra of fresh sample was taken a day after the sample preparation and then the same sample was investigated seven months later (aged). To be able to study the chemical environment of bulk Cu atoms without surface contamination we bombarded both, fresh and aged, samples with Ar$^+$ ions using same sputtering parameters. Presented core-level spectra were measured when the C 1s signal had almost vanished from the overview spectrum. The core-level spectra of Cu 2p$_{3/2}$ and O 1s of fresh (○) and aged (●) GdBCO
Comparison of Cu $2p_{3/2}$ core-levels and Cu satellite spectra of fresh and aged GdBCO show that the amount of Cu$^{2+}$ has decreased as a function of time. The black line (residue) describes the difference between the Cu $2p$ spectra of fresh and aged samples. From the O 1s spectra presented in the inset of figure 5 it can be seen that the oxygen contamination (high BE feature) is much higher for the aged GdBCO despite the similar sputtering treatment of the samples.

Two features can be clearly distinguished also in the O 1s spectra of both measurements (inset in figure 5). The low BE feature at about 529 eV is caused by Cu-O planes and Cu-O chains and the component at high BE side (531 eV) is due to oxygen contamination [27, 29, 33]. The intensity changes of the CuO satellite in aged and fresh sample strongly suggests that the amount of CuO has decreased. The intensity ratio ($I_{CuO}/I_{Cu_2O}$) calculated by comparing the areas of the CuO satellite and Cu $2p_{3/2}$ signal of Cu$_2$O of fresh and aged GdBCO changed from about 0.5 to 0.2, respectively. Two features can be clearly distinguished also in the O 1s spectra of both measurements (inset in figure 5). The low BE feature at about 529 eV is caused by Cu-O planes and Cu-O chains and the component at high BE side (531 eV) is due to oxygen contamination [27, 29, 33].

The effect of ageing as a loss of Cu$^{2+}$ can be observed as a decreased intensity of Cu $2p$ satellite at the binding energy range from 940 to 945 eV. Also the slight narrowing of the Cu $2p_{3/2}$ core-level caused by conversion of CuO (Cu$^{2+}$) to Cu$_2$O (Cu$^{1+}$) is due to the same effect. Despite the removal of carbon contamination by sputtering, the O 1s spectrum of aged sample shows that the oxygen contamination has increased as a comparison to the fresh sample. This suggests that the oxygen from the surface can diffuse into the structure being more difficult to
4. Discussion

There seems to be a good agreement between the x-ray diffraction peak intensity ratio changes and decrease of $J_c$ and $T_c$: the step between the fresh and 1 month old data in both the GdBCO films is rather steep in $I(005)/I(001)$-ratios (figure 2) and in $J_c$ (figure 4 (c)&(d)), and later measurements the changes are smaller or they might be even normal variation between measurements in uc-GdBCO. These two phenomena were related to change in oxygen content [15]. The XPS measurements agree well with these results. The changes in lattice parameter $c$ is partly in contrast with former ones, except for Au-GdBCO, but we note here that the $c$ parameter depends on several variables, so the decrease might arise from a relaxation of an other variable than oxygen content and further, this kind of variation in $2\theta$ is so small, 0.05° that it might be impossible to be accurately measured in such a long period of time. There was no major change in $(2\theta, \phi)$-scans and no change in the size of low field plateau of $J_c$, nor change in high field curve-shape of $J_c$ was seen. Hence, we conclude that the pinning structure has not changed. Also, no major impurity phase development was found in all the films except Au-GdBCO. The reduction of $M'$ correlates with that, because both indicate the diminution of the volume of superconducting material. Thus, we conclude that the decrease of $T_c$ and $J_c$ are originated by release of oxygen.

The reason for release of oxygen in GdBCO, when no such a phenomenon is present in YBCO, is unclear, but the reason might lie in the extra stacking faults present in GdBCO but not in YBCO. These stacking faults can be for example an extra Gd-layer [13] which result in an edge dislocation. The diffusion of oxygen between oxygen vacancies is rather slow in $c$-direction, but fast in $ab$-plane, latter being several magnitudes higher [34]. Further, the diffusion of oxygen through disorders has been estimated to be in the same magnitude as the diffusion in $ab$-plane [35]. Since GdBCO has more edge dislocations, it is easier for oxygen to move in $c$-direction because of the shifted Ba- and Cu-oxide layers. Our previous work supports this explanation: we have seen a similar aging effect in YBCO grown on STO (110) films, where $ab$-planes are perpendicular to the substrate surface, resulting in faster oxygen release [36]. There is also a possibility that a protective layer on YBCO is formed in ambient air but not on GdBCO, but we note here that if this was the case, it would not explain why there is no oxygen dissolution in Au-YBCO, where this kind of layer forming is restrained by the gold layer which is known to allow oxygen diffusion. The Au-sputtering seems to induce a development of a surface layer of weaker superconducting properties in both samples. This is seen in widening of the transition (figure 3 (b)&(d)). There seems to be also a correlation between the lower amount of secondary phase (figure 3) and less dramatic decrease of $J_c$ (table 1 and figure 4) in GdBCO in comparison to YBCO. The development of the secondary phase may be related to the reduced oxygen content which is seen as an increase in $c$ parameter (figure 1 (b)) and in $I(005)/I(004)$ intensity ratio (figure 2 (a)) as well as a decrease in $I(005)/I(007)$ intensity ratio (figure 2 (b)). The reduction of oxygen may be due to the diffusion of Au inside the YBCO and GdBCO material, which is seen for melt-textured YBCO [37]. The reason why this phenomenon seems to be stronger for YBCO than for GdBCO is probably resulted by lower oxygen content of the YBCO samples, which is indicated by larger difference of $T_c$ to its single crystal value, which are 92 K and 92.5 K for YBCO and GdBCO, respectively [38]. Since the $T_c$ of the YBCO samples is in the negative slope regime (see figure 16 in ref. [15]) and uc-GdBCO and Au-GdBCO are in the high $T_c$ plateau of $\delta \leq 0.2$, the reduction of oxygen is more dramatic for these YBCO samples. Also, the irreversibility resulted by barrier effect may play a small role in low magnetic regime as calculated by Carty et al. [39]. They showed that coating the superconductor with normal metal instead of insulator reduced the irreversibility and thus $J_c$. Moreover, they also predicted that introduction of a layer of
material with lower superconducting properties reduces the barrier irreversibility even further. We note that this might be the case here, if the assumption of gold removing the oxygen in a surface layer is correct. However, this surface barrier is probably significant only in vicinity of $H_{c1}$, because in the concerned films there is surface roughness and twin boundaries [39].

Also, the reason why the oxygen release is faster in Au-GdBCO than in uc-GdBCO is unclear. We have thought of two possible explanations. The first is that Au tends to form islands rather than distribute smoothly on the surface. These formed islands may produce cracks in the films. The island structure has been seen in atomic force microscopy on our Au-GdBCO films. This possibility is suppressed by the fact that the gold sputtering was made at room temperature, so the gold layer is not attached tightly on the surface of the film. On the other hand, sputtering has a negative influence on $T_c$ and $J_c$ which might support this explanation, but only if gold layer has only minor or no influence on charge distribution in the surface of the superconductor. The second possibility is gold acting as a catalyst. There are some indications in literature of nanosized Au behaving as a catalyst for carbon monoxide and hydrogen oxidation at low temperatures [40]. In addition, the well known fact is that YBCO and GdBCO surfaces are usually rough, root-mean-square roughness being even 5 nm in GdBCO [21, 41], and this would yield to rough Au-interfaces, whose pore size is in nanoscale – an ideal Au catalyst interface.

We note here that even if it seems that Au is a poor cap layer, this might hold only for certain substrates, since the surface roughness depends on substrate material. So, some further investigations are needed in order to state if this phenomenon is universal or if it is substrate or deposition condition and method dependent. Furthermore, various cap-layers should be inspected.

5. Conclusions
We have systematically compared time dependence of magnetic and structural properties in uncoated and gold coated YBCO and GdBCO thin films. The YBCO films did not show any major change in ambient air within 5–6 months measurement period. The uncoated GdBCO showed some decrease of $J_c$ during the first 1–2 months and gold coated GdBCO a rapid decrease of $T_c$ and $J_c$ in the whole time period. This phenomenon might be related to higher stacking fault density in GdBCO in comparison to YBCO and the rapid phenomenon in gold coated GdBCO due to gold layer forming cracks in GdBCO film or gold being a catalyst.

6. Acknowledgements
The authors wish to acknowledge Wihuri foundation, Finland for financial support and G. Anderson, Uppsala University, Sweden for useful discussion.

References
[1] Iguchi T, Araki T, Yamada Y, Hirabayashi I and Ikuta H 2002 *Supercond. Sci. Technol.* **15** 1415
[2] Takahashi K, Yamada Y, Konishi M, Watanabe T, Ibi A, Muroga T, Miyata S, Shiohara Y, Kato T and Hirayama T 2005 *Supercond. Sci. Technol.* **18** 1118
[3] Song S H, Ko K P, Ko R K, Song K J, Moon S H and Yoo S I 2007 *Physica C* **463-465** 497
[4] Yamada Y, Takahashi K, Kobayashi H, Konishi M, Watanabe T, Ibi A, Muroga T, Miyata S, Kato T, Hirayama T and Shiohara Y 2005 *Appl. Phys. Lett.* **87** 132502
[5] Ibi A, Fukushima H, Yamada Y, Miyata S, Kuriki R, Takahashi K and Shiohara Y 2006 *Supercond. Sci. Technol.* **19** 1229
[6] Kinoshita A, Takahashi K, Kobayashi H, Yamada Y, Ibi A, Fukushima H, Konishi M, Miyata S, Shiohara Y, Kato T and Hirayama T 2007 *Physica C* **463-465** 630
[7] Shiohara Y, Yoshizumi M, Izumi T and Yamada Y 2008 *Supercond. Sci. Technol.* **21** 034002
[8] Takahashi K, Kobayashi H, Yamada Y, Ibi A, Fukushima H, Konishi M, Miyata S, Shiohara Y, Kato T and Hirayama T 2006 *Supercond. Sci. Technol.* **19** 924
[9] Lee S, Chikumoto N, Yokoyama T, Machi T, Nakao K and Tanabe K 2009 *IEEE T. Appl. Supercond.* **19** 3192 golden cap layer.
[10] Hanyu S, Miura T, Ijima Y, Igarashi M, Hanada Y, Fuji H, Kakimoto K, Kato T, Hirayama T and Saitoh T 2008 J. Phys. : Conf. Series 97 012273

[11] Fukushima H, Ibi A, Takahashi H, Kuriki R, Miyata S, Yamada Y and Shiohara Y 2007 Physica C 463-465 501

[12] Fukushima H, Ibi A, Takahashi H, Kuriki R, Miyata S, Yamada Y, Shiohara Y, Kato T and Hirayama T 2007 IEEE T. Appl. Supercond. 17 3367

[13] Haberkorn N, Lovey F, Condó A M and Guimpel J 2005 J. Appl. Phys. 98 123505

[14] Jorgensen J D, Veal B W, Paulikas A P, Nowicki L J, Crabtree G W, Claus H and Kwok W K 1990 Phys. Rev. B 41 1863

[15] Ye J and Nakamura K 1993 Phys. Rev. B 48 7554

[16] Li T, Wang B, Dai H, Du Y, Yan H and Liu Y 2005 J. Appl. Phys. 98 123505

[17] Higashikawa K, Kiss T, Inoue M, Imamura K, Nakamura T, Awaji S, Watanabe F, Fukushima H, Yamada Y and Shiohara Y 2009 IEEE T. Appl. Supercond. 19 1621 coil simulation, the silver capped GdBCO coated conductors are used.

[18] Paik K W and Mogro-Campero A 1994 IEEE Transactions on Components, Packaging and Manufacturing Technology–Part B 17 435

[19] Kula W, Xiong W, Sobolewski R and Talvacchio J 1995 IEEE T. Appl. Supercond. 5 1177

[20] Raittila J, Huhtinen H, Paturi P and Stepnan Y P 2002 Physica C 371 90

[21] Schlesier K, Huhtinen H, Paturi P, Stepnan Y P and Laiho R 2009 IEEE T. Appl. Supercond. 19 3407 aSC paper, Chicago.

[22] Peurla M, Huhtinen H and Paturi P 2005 Supercond. Sci. Technol. 18 628

[23] Paturi P, Ijala M and Huhtinen H 2008 J. Appl. Phys. 103 123907

[24] Bean C P 1962 Phys. Rev. Lett. 8 250 beam model (original), critical state model

[25] Bean C P 1964 Reviews of Modern Physics 36 31 beam model (original), critical state model

[26] Wiesinger H P, Sauerzopf F M and Weber H W 1992 Physica C 203 121

[27] Weaver J H, Meyer III H M, Wagener T J, Hill D M and Gao Y 1988 Phys. Rev. B 38 4668

[28] Behner H, Rührnschopf K, Rauch W and Wedler G 1993 Applied Surface Science 68 179

[29] Teterin Y A, Sosulnikov M I and Petrov Y A 1994 Journal of Electron Spectroscopy and Related Phenomena 68 469

[30] Beyer J, Schuring T, Menkel S, Quan Z and Koch H 1995 Physica C 246 156

[31] Ghijsen J, Tjeng L H, van Elp J, Eskes H, Westerink J, Sawatzky G A and Czyzyk M T 1988 Phys. Rev. B 38 11322

[32] Jernigan G G and Somorjai G A 1994 Journal of Catalysis 147 567

[33] Hartmann A, Russell G J and Taylor K N R 1993 Physica C 205 78

[34] Rothman S J, Routbort J L, Welp U and Baker J E 1991 Phys. Rev. B 44 2326

[35] Kursumovic A, Berghuis P, Dediu V, Evetts J E, Matacotta F C and Wagner G A 2000 Physica C 331 185 diffusion at 600 C.

[36] Paturi P, (Unpublished)

[37] Veretnik D and Reich S 1994 Physica C 223 227

[38] Cardwell D A and Babu N H 2006 Physica C 445-448 1

[39] Carty G J, Machida M and Hampshire D P 2005 Phys. Rev. B 71 144507

[40] Haruta M, Yamada N, Kobayashi T and Iijima S 1985 Journal of Catalysis 115 301

[41] Miyachi K, Sudo K, Ichino Y, Yoshida Y and Takai Y 2003 Physica C 392-396 1261