IOP Publishing Mater. Res. Express 5 (2018) 056001 https://doi.org/10.1088/2053-1591/aabf51

Materials Research Express

RECEIVED
14 March 2018

REVISED
3 April 2018

ACCEPTED FOR PUBLICATION
19 April 2018

PUBLISHED
2 May 2018

PAPER

Very-high thermal and electrical conductivity in overpressure-processed $Bi_2Sr_2CaCu_2O_{8+x}$ wires

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Keywords: Bi-2212, RRR, thermal conductivity, silver, Bi2212, overpressure

Abstract

The residual-resistivity ratio (*RRR*) of the normal-metal matrix is a key parameter for the electrical and thermal stability of technical superconductors. In $Bi_2Sr_2CaCu_2O_{8+x}$ (Bi-2212) round wires, the precursor powders are embedded in a Ag matrix without any diffusion barrier, and elemental diffusion from the superconducting filaments into the Ag might be expected to contaminate the matrix during the melt processing required for high critical current density development. This work shows that the overpressure processing, which is adopted to enhance the critical current performance, improves the thermal and electrical conductivities of the conductor, too. In the case of wires reacted with a standard processing performed in 1 bar O_2, the *RRR* of the Ag matrix is about 90, in spite of the simple conductor design that does not include diffusion barriers. Increasing the total reaction pressure to 100 bar improves the *RRR* to about 200. The differences in *RRR* reflect on the thermal conductivity of the whole conductor, which has been investigated in magnetic fields up to 19 T.

1. Introduction

The increase of mass density, electrical connectivity and critical current density (J_C) induced by overpressure processing has made $Bi_2Sr_2CaCu_2O_{8+x}$ (Bi-2212) a credible candidate for solenoids and accelerator magnets able to generate magnetic fields unattainable with low-temperature superconductors [1, 2]. Whether Bi-2212 can be preferred to other high-temperature superconductors (HTS) for high-field applications depends also on the mechanical, thermal and electrical stability of the conductor [3–5]. The residual-resistivity ratio (*RRR*) of the normal-metal matrix is a key parameter for both the thermal and the electrical properties. In Bi-2212 wires, the thermal conduction at cryogenic temperatures is dominated by the contribution of the Ag matrix surrounding the Bi-2212 filaments, because of the low thermal conductivity (κ) of the superconducting filaments and of the outer sheath used to strengthen the conductor [6–8]. In normal metals, electron scattering processes determine the thermal conduction at low temperature (T) and a direct correlation between the *RRR* and κ is observed: the higher the *RRR*, the higher the κ [9]. The magnetic field lowers the electron mobility affecting the thermal conductivity [9–11]. The in-field thermal properties are thus extremely important in view of the use of the wires in high-field magnets. On a more general note, the *RRR* is relevant for the protection of superconducting magnets in case of quench, as the Joule heating generation term is proportional to the electrical resistivity (ρ) of the normal matrix [12, 13]. An open issue about Bi-2212 conductors is to what extent the Ag matrix is contaminated during the heat treatment due to Bi-2212 element diffusion. Among the elements present in $Bi_2Sr_2CaCu_2O_{8+x}$, Cu has the highest solubility in Ag [14]. Contrary to the case of Nb-Ti and Nb_3Sn, the *RRR* of the matrix in HTS technical conductors cannot be evaluated from an electrical resistivity measurement performed on the whole conductor. Due to the superconducting transition at high T, it is not possible to measure the residual ρ of the matrix. In the case of $REBa_2Cu_3O_{7-x}$ coated conductors, where the stabilization is performed by soldering or electroplating Cu on the tape, the stabilizer can be delaminated from the tape allowing direct measurement of its *RRR* [10]. In Bi-2212 wires, the superconducting filaments are embedded in a Ag matrix which makes separation of the stabilizer from the superconductor challenging. In a prior work, Li *et al* evaluated the *RRR* of the matrix in Bi-2212 wires processed with a non-standard partial-melt-processing, specifically designed to generate critical-current-depressed samples with very little superconducting phase [6]. This work studies the *RRR* of Ag and κ of fully-reacted high-J_C conductors given standard partial-melt-process heat treatment at 1, 10 and 100 bar total pressure, the reactions in each case being carried out at 1 bar pO_2. κ has been investigated in magnetic fields up to 19 T. The *RRR* of the metal matrix has been assessed by measuring the electrical resistance (R) of short pieces of conductor from which the superconducting filaments have been removed by chemical etching. This has allowed us to quantify the effects of the overpressure heat treatment on the low-temperature electrical and thermal conductivity properties.

2. Methods

Three Ag-0.2 wt% Mg (AgMg) reinforced 0.8 mm-diameter Bi-2212 wires composed of 37×18 filaments embedded in a Ag matrix have been investigated. Samples were extracted from the same batch (manufacturer: Oxford Superconducting Technologies, billet number: ppm130723-2) and reacted at the National High Magnetic Field Laboratory under different total pressures of 1 (Bi-2212_1 bar), 10 (Bi-2212_10 bar) and 100 bar (Bi-2212_100 bar), at a fixed O_2 partial pressure of 1 bar, with a maximum T of 890 °C. The thermal and electrical conductivity properties have been investigated at the University of Geneva. κ has been measured using a setup specifically designed for high-field measurements in technical superconductors [10, 11]. Heat is supplied at one end of the sample to establish a T gradient along it. The gradient is measured by means of two Cernox® bare chips that are directly glued on the sample and that are calibrated against a reference sensor during each measurement. The measurement is performed once the steady state heat flow is established. The measurement uncertainty is about 10%, the dominant factor being uncertainty in the distance measurement between the two Cernox® bare chips. κ has been measured in fields up to 19 T, applied perpendicularly to the heat-flow direction. This orientation is the most relevant for superconducting magnets and gives the highest field-induced effects [9, 10]. The *RRR* was determined by a 4-wire R measurement performed at zero field using a low-noise probe for electrical transport measurements [15]. A Keithley 2400 source-meter, which allows measuring the actual current in the circuit, was used as a current source. An excitation current of 0.1 A was chosen in order to avoid heating effects. The voltage drop across the sample has been amplified by a factor 10000 by means of a EM-Electronics nanovolt amplifier (no filter used) and measured with a Keithley 2182A nanovolt-meter.

3. Results

The experimental $\kappa(T)$ curves of the samples reacted at 1, 10 and 100 bar are presented in panels (a), (b) and (c) of figure 1, respectively. κ was measured in the T range $\approx$ 4–40 K at $B = 0, 1, 7$ and 19 T. Two additional data points were taken at $T \approx 55$ K and ≈ 77 K in zero field. Dashed lines have been added to guide the eye. The $\kappa(T)$ curves at $B = 0$, 1 and 7 T exhibit a clear peak whose intensity lowers with increasing field. At 19 T the peak is barely distinguishable and $\kappa(T)$ increases almost monotonically. The pairs of values (T_{peak}, κ_{peak}), which identify the peak position at $B = 0, 1, 7$ T, for the three investigated samples, are plotted in the inset of figure 1(c) along with the best-fit straight line. This graph shows the correlation between the position and the magnitude of the peak: the higher is T_{peak}, the lower is κ_{peak}. For an easier comparison, the values of $\kappa_{peak}(0\ \mathrm{T})$, i.e. the maximum of the $\kappa(T)$ curve at $B = 0$, have been reported in table 1. $\kappa_{peak}(0\ \mathrm{T})$ is raised by ≈ 135 % on increasing the heat-treatment pressure from 1 to 100 bar. The field-induced reduction of κ is more pronounced for wires reacted at higher pressures. In table 1, we have reported κ measured at 19 T and 20 K. This temperature corresponds approximatively to the beginning of the $\kappa(T)$-curve sector that is weakly dependent on T. These data indicate that increasing the reaction pressure from 1 to 100 bar results in a 25% improvement of κ at high fields.

In order to correlate the thermal conductivity properties to the *RRR* of the Ag matrix, we removed the superconducting filaments from short conductor pieces, dissolving the Bi-2212 in glacial acetic acid. The chemical etching, performed at room temperature, lasted $\approx$ 8 days, magnetically stirred with a frequency of $\approx$ 2 turns per second. Following this protocol, it is possible to remove the Bi-2212 from $\approx$ 2 mm-long conductors, without degrading the wire matrix that is inert to acetic acid. However, we did not succeed in completely dissolving the superconducting filaments from longer samples, even extending the duration of the process by several days. A 4-wire $R(T)$ measurement on high-*RRR* short metallic samples is highly demanding in measurement sensitivity because in our case, R as low as ~ 100 nΩ has to be measured. The residual, R_{Res}, and room-temperature electrical resistance, as measured in the etched Bi-2212_100 bar sample, are reported in figure 2. The *RRR* of the non-superconducting fraction of the conductor (Ag and AgMg), defined as

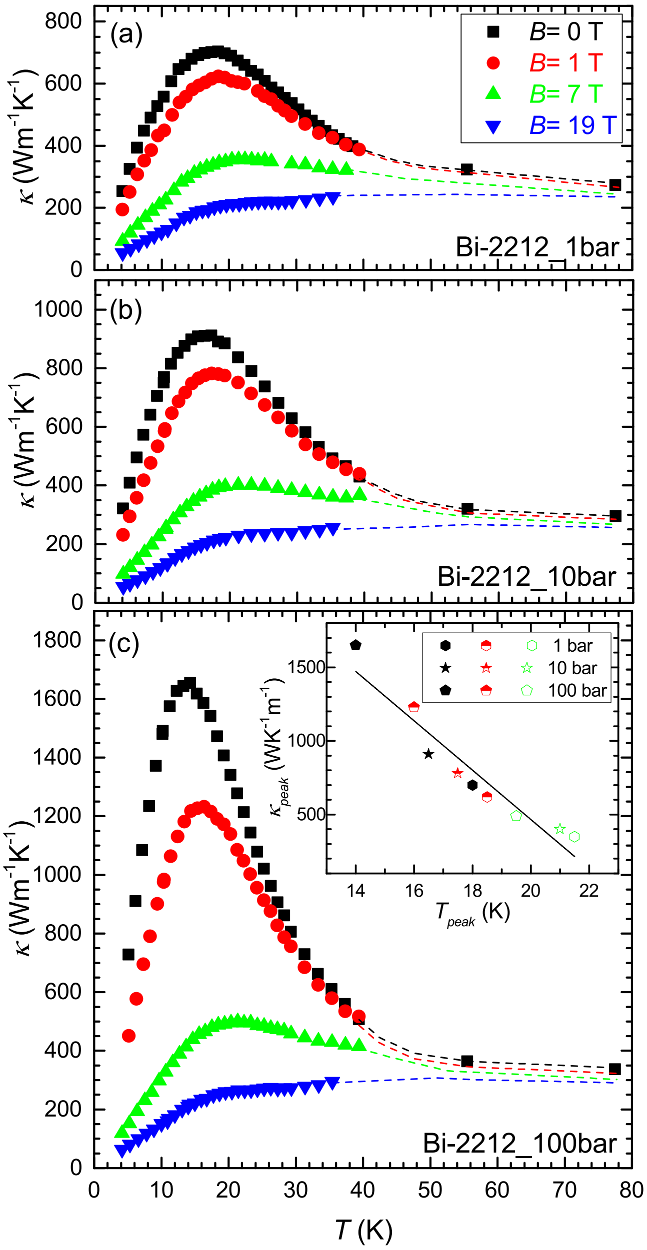

Figure 1. Temperature dependence of the thermal conductivity at different fields for Bi-2212 wires reacted at 1 (a), 10 (b) and 100 bar (c). Dashed lines are guides to the eye. The inset in (c) reports the coordinates of the $\kappa(T)$-curve peak at 0 T (full symbols), 1 T (half-full symbols) and 7 T (open symbols), along with the best-fit straight line.

Table 1. Structural, thermal and electrical properties of the investigated Bi-2212 conductors.

	Bi-2212_1 bar	Bi-2212_10 bar	Bi-2212_100 bar
κ_{peak}(0 T)	700 $\mathrm{Wm^{-1}K^{-1}}$	910 $\mathrm{Wm^{-1}K^{-1}}$	1650 $\mathrm{Wm^{-1}K^{-1}}$
κ(20 K, 19 T)	210 $\mathrm{Wm^{-1}K^{-1}}$	225 $\mathrm{Wm^{-1}K^{-1}}$	260 $\mathrm{Wm^{-1}K^{-1}}$
Filament fraction ($s_{fil.}$)	0.22	0.22	0.22
Silver fraction (s_{Ag})	0.54	0.54	0.54
Silver-alloy fraction (s_{AgMg})	0.24	0.24	0.24
RRR of the normal-metal matrix	95	110	220
RRR of Ag	90	104	208

$R(300\ \mathrm{K})/R_{Res}$, is ≈ 220. As the relative amount of Ag and AgMg in the cross-section is known, the *RRR* of Ag can be determined considering that, at low T, $\rho_{Ag} \ll \rho_{AgMg}$ whilst at 300 K $\rho_{Ag} \approx 16.1\ \mathrm{n\Omega\ m}$ and $\rho_{AgMg} \approx 19.7\ \mathrm{n\Omega\ m}$ [6]. The parallel-resistor calculation leads to an *RRR* of ≈ 208 for the matrix Ag. Table 1 summarizes the *RRR* of the non-superconducting fraction of the conductor and that of Ag for all the investigated wires. The same data have

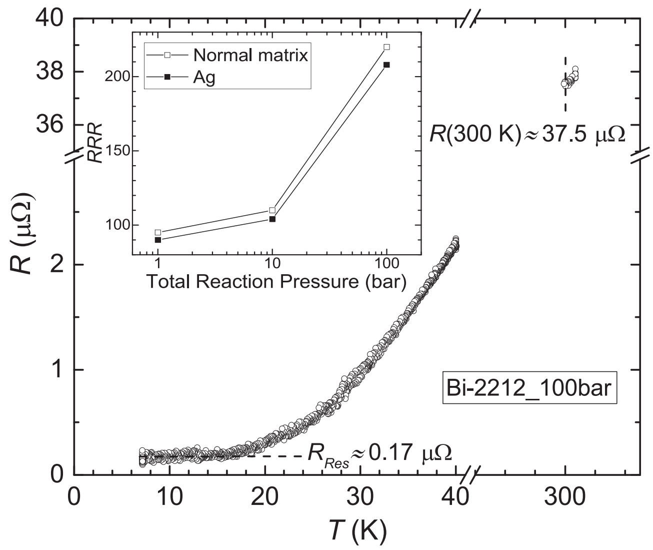

Figure 2. Low- and room-temperature electrical resistance measured on a 2 mm-long Bi-2212 conductor reacted at 100 bar, in which the superconducting filaments have been dissolved away in glacial acetic acid. The inset shows the dependence of the normal-matrix and Ag *RRR* on the heat treatment pressure.

been plotted in the inset of figure 2. Both κ and *RRR* increase with the overpressure, *RRR* more than doubling from ≈ 90 in the 1 bar reacted sample to ≈ 208 in the 100 bar sample. This result shows that the heat-treatment pressure has an influence on the contamination of the Ag matrix.

4. Discussion

The thermal transport along composite conductors can be treated with the formalism adopted in the case of resistances connected in parallel. The overall κ is given by the weighted sum of the thermal conductivity of each component, κ_i, with weight, s_i, corresponding to the cross-section fraction occupied by the i^{th} component: $\kappa = \sum \kappa_i s_i$. Table 1 lists the filament (Bi-2212 and voids, $s_{fil.}$), Ag (s_{Ag}), and AgMg (s_{AgMg}) cross-section fractions for the investigated wires. κ of Bi-2212 is below ≈ 4 WK^{-1}m^{-1} at $T \lesssim 150$ K [7]. From the κ values reported in figure 1, we deduce that its contribution to the overall κ is negligible. κ of AgMg used in the production of Bi-2212 wires has been reported in [6]. Its contribution to the overall κ is less than $\approx 10\%$ at $T \lesssim 40$ K and decreases at lower T. Figure 3 shows $\kappa_{Ag}(T)$ for the three investigated samples, as evaluated considering that $\kappa_{Ag}(T) \approx (\kappa(T)\text{-}\kappa_{AgMg}(T)s_{AgMg})/s_{Ag}$, using the experimental $\kappa(T)$ of figure 1 and s_i values reported in table 1 and $\kappa_{AgMg}(T)$ from [6]. In the same plot we have included the $\kappa(T)$ curves for Ag samples with different *RRR* from the literature [6, 8].

The measured $\kappa(T)$ and *RRR* of Ag for the Bi-2212_100 bar sample are consistent within the experimental accuracy with the results shown by Li *et al* on a stand-alone pure Ag sample [6]. Their sample was heat treated using a standard Bi-2212 heat treatment schedule in a total pressure of 1 bar O_2 and an *RRR* of 214 was measured (blue line in figure 3). Since the stand-alone sample is from the silver stock used in wire production, we infer that: (i) the excursion to high temperature removes the matrix internal stresses after the deformation process; (ii) matrix poisoning when reacting the wire at 100 bar is very low. On the other hand, element contamination effects cannot be neglected when the conductor is reacted at pressures $\lesssim 10$ bar. The lowest *RRR* of Ag (≈ 90) has been measured on the conductor reacted at 1 bar. This *RRR* reduction of a factor of ≈ 2 is not so dramatic if we consider that, in the case of Nb_3Sn wires, a complex conductor layout that includes reaction barriers around the filaments is necessary to keep the *RRR* above ≈ 100 [16].

Figure 4 shows the correlation between the *RRR* and the maximum of the $\kappa(T)$ curve at $B = 0$ for Ag. The dashed line has been added to guide the eye. Considering the complexity of the procedure to measure $R(T)$ on the etched short wires, this plot provides an alternative practical method to estimate the *RRR* of the Ag matrix from a $\kappa(T)$ measurement performed at $B = 0$ on the whole conductor. Indeed, κ_{Peak} of Ag can be estimated considering that $\kappa_{Ag} \approx \kappa / s_{Ag}$, in view of the fact that AgMg gives only second order corrections to κ at $T \lesssim 40$ K.

The reduction of κ upon increasing the magnetic field can be qualitatively understood considering that the thermal conductivity of normal metals at low temperatures is proportional to the electron mean free path. The latter decreases with the magnetic field because of the action of the Lorenz force on the charge carriers. The

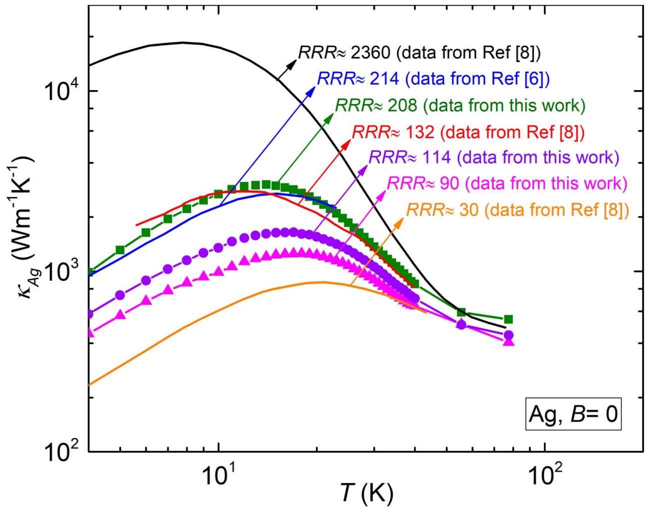

Figure 3. Temperature dependence of the thermal conductivity of Ag samples of different purity.

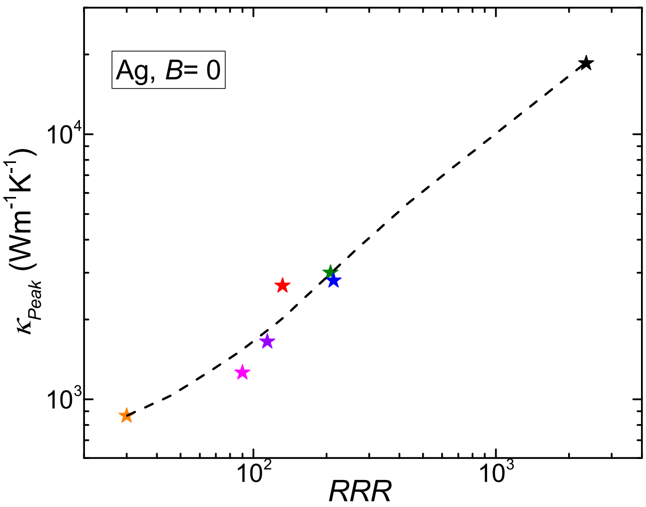

Figure 4. Correlation between the RRR and the maximum of the $\kappa(T)$ curve at $B = 0$ for Ag. The symbol colors are in accordance with the results of figure 3; the dashed line is to guide the eye.

Wiedemann-Franz law defines quantitatively the correlation between the thermal conductivity and the electrical resistivity in metals: $\kappa\rho = LT$. L is the Lorenz number, which at $T \approx 0$ K assumes the value $L_0 = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2 \approx 2.44 \times 10^{-8}\ \mathrm{W\Omega K^{-2}}$, where k_B is the Boltzmann constant and e the electron charge [17]. Predictions of the Wiedemann-Franz law are in good agreement with experiments at low temperatures and zero magnetic field, provided that the phonon contribution to thermal transport is negligible and that electron scattering processes are elastic [18, 19]. In the case of Ag, very few studies are present in the literature and show that L varies with T going from $\approx 2.4 \times 10^{-8}\ \mathrm{W\Omega K^{-2}}$ at 2 K to $\approx 1 \times 10^{-8}\ \mathrm{W\Omega K^{-2}}$ at 15 K [8, 20]. To the best of our knowledge, there are no published data over a wider range of cryogenic temperatures or at fields higher than 0.5 T [8]. The field-induced reduction of κ can be viewed in the framework of the Wiedemann-Franz law as a consequence of the increase of ρ due to magneto-resistance effects [6, 21].

Comparison of the present results with those of Li *et al* [6] is interesting. Both our and their study show that extremely high thermal and electrical conductivities can be obtained after reaction. Li *et al* showed explicit evidence that Cu dissolves in the Ag and they also found copper oxide at the surface after an excursion to 890 °C. In their experiment, they gave an extended heat treatment at 890 °C and then promptly quenched their samples so as to have almost no superconducting phase, thus being able to measure the RRR of the full wires. Curiously they found that extending the 890 °C heat treatment time from 1 to 48 h led to monotonically better electrical conductivity, the RRR of the full wire rising from about 350 at 1 h to about 440 after 48 h. Such a long period in the melt is expected to be strongly degrading to J_C [22] but it is a good way to encourage an equilibrium dissolution into the Ag. Their conclusion that the thermodynamically stable end state is for the Cu to diffuse into the Ag matrix and then to the surface where it precipitates as an oxide, could also explain why a full optimization heat treatment at higher total pressure produces lower electrical resistivity and higher thermal conductivity. We know that higher overpressure better densifies the Bi-2212 filaments and it must also enhance the diffusional connectivity of the filaments to the matrix. It is a striking outcome of this study that higher overpressure not only enhances J_C but also the electrical and thermal conductivity of the Ag matrix around each filament. However, even the lowest *RRR* of Ag (≈ 90) measured on the conductor reacted at 1 bar is still good, especially in comparison to Nb_3Sn wires, where diffusion barriers around the superconducting filaments are necessary to keep the *RRR* above ≈ 100 [16]. A complete understanding of the mechanisms behind the improved thermal and electrical properties demands for a deep investigation of the microstructural properties of the matrix, as well as of the chemical diffusion processes from the filaments to the matrix. We consider that this goes beyond the scope of the present paper. In the case of wires reacted at 1 bar, energy dispersive x-ray spectrometry has been unable to detect Cu signal in the Ag matrix above the detection limit of 0.1 at% [6]. This suggests that the observed differences in *RRR*, if due to Cu, are determined by variations of the Cu content in the Ag matrix < 0.1 at%, which are very difficult to detect.

5. Conclusion

We investigated the thermal conductivity of overpressure-processed Bi-2212 wires in magnetic fields up to 19 T. κ is raised up to $\approx 135\%$ at $B = 0$ and $\approx 25\%$ at $B = 19$ T on increasing the heat-treatment pressure from 1 to 100 bar. The enhancement of the thermal conductivity is due to a rise of the *RRR* of the Ag matrix, which passes from ≈ 90 to ≈ 208 on increasing the reaction pressure from 1 to 100 bar. Results very similar to those obtained in the wire reacted at 100 bar, both for κ and *RRR*, were previously reported for a stand-alone Ag sample from the stock used in the wire production, heat treated using a standard Bi-2212 heat treatment. From the comparison, we infer that matrix poisoning when reacting the wire at 100 bar is very low. We also proposed a practical method to estimate the *RRR* of the Ag matrix from a $\kappa(T)$ measurement performed at $B = 0$ in the reacted conductor. A main outcome of this work is that a higher overpressure limits the Ag-matrix contamination during the wire heat treatment, providing both the highest J_C and the highest thermal and electrical conductivity with great benefit to the thermal and electrical conductivity properties of the conductor.

Acknowledgments

The authors acknowledge Davide Matera, Enrico Giannini, Gaia Grimaldi and Angela Nigro for valuable discussions, Damien Zurmuehle for technical assistance. Financial support was provided by the SNSF (Grant No. PP00P2 144673) and by FP7 EuCARD-2 http://eucard2.web.cern.ch. EuCARD-2 is cofounded by the partners and the European Commission under Capacities 7th Framework Programme, Grant Agreement 312453. The work performed at the National High Magnetic Field Laboratory (NHMFL) is supported by the US DOE Office of High Energy Physics under grant number DE-SC0010421, and by the NHMFL which is supported by National Science Foundation through NSF/DMR-1157490 and NSF/DMR-1644779 and the State of Florida. A Leo acknowledges funding support from the Short Term Mobility Program of the Italian National Research Council (CNR).

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