Critical current behavior of superconducting MoN and Mo$_3$Sb$_7$ microfibers

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We present the transport and critical current measurements on carbon microfibers coated with 40-nm of polycrystalline δ-MoN and on carbon microfibers coated with 160 nm of Mo$_3$Sb$_7$. In each case the coatings where synthesized directly onto the 6-μm diameter carbon fibers. The superconducting transition temperature of the MoN microfibers was $T_c \sim 13.1$ K, which is the highest temperature reported in any thin film form and is higher than what was reported for stoichiometric δ-MoN, produced by high pressure synthesis. The transition temperature of the Mo$_3$Sb$_7$-coated microfibers $T_c = 7.5$ K was significantly higher than that observed in powder samples. Near the transition temperature T_c, the critical current density J_c for both systems was well described by the power-law form $[1-(T/T_c)^2]^\alpha$, where $\alpha = 1.5$ is the Ginzburg–Landau exponent. We extrapolated $J_c(0) \approx 5 \times 10^7$ A/cm^2 for the MoN microfibers and $J_c(0) \approx 2.5 \times 10^5$ A/cm^2 for the Mo$_3$Sb$_7$ fibers.

I. INTRODUCTION

Transition metal-based superconductors have been an historically important class of materials, primarily due the fact that the A15 intermetallics, such as Nb$_3$Sn, became widely used in high magnetic field applications, most notably in the windings of superconducting solenoids.[1] Although the most extensive research has been carried out on niobium intermetallics, there has been a recent renewal of interest in two particular molybdenum-based superconductors. The first is molybdenum nitride which exhibits a number of interesting physical properties. For instance, MoN can be used to form high-hardness refractory films making it potentially useful for microelectromechanical components, tribological applications, and/or protective coatings.[2,3] These, in combination with its relatively high transition temperature $T_c \sim 13$ K, provide ample motive for further development.[4] Indeed, it is believed that its metastable cubic phase ($B1$-MoN) will have a $T_c \sim 30$ K, although this has yet to be demonstrated.[5,6] The second compound is Mo$_3$Sb$_7$, which was recently classified as a strong spin-fluctuation superconductor.[7,8] It is believed to be similar to the nonconventional superconductor MgCNi$_3$, which also exhibits strong spin fluctuations due to its proximity to a ferromagnetic ground state. In both these latter systems, strong spin fluctuations alter the superconducting ground state properties in nontrivial ways.[8,9] Here we present transport critical current measurements of annular MoN and Mo$_3$Sb$_7$ fibers as a function of temperature. We show that the scaling behavior of J_c near the transition temperature T_c is well described by a Ginzburg-Landau (GL) form[10] in both systems. However, the magnitude of the critical current density in the Mo$_3$Sb$_7$ fibers is an order of magnitude lower than what would be expected from its transition temperature. We speculate that this may be a ramification of an anomalously large spin-fluctuation amplitude.

II. SAMPLE PREPARATION

Annular MoN and Mo$_3$Sb$_7$ films were formed on Mo-coated carbon fibers obtained from JW Composites, LC.[11]

The commercial fibers consist of a 6-μm diameter carbon core onto which a 40-nm-thick film of Mo has been deposited via a proprietary chemical vapor deposition process. We formed MoN by reacting the Mo-coated carbon fibers in a 1 atm stream of ammonia gas (NH$_3$) at 850–1000 °C for different periods. Exposures at 900 °C for 90 min resulted in the samples with the best superconducting properties. The moly-antimonide coatings were formed by first sealing the commercial Mo-coated fibers in an evacuated quartz tube with a small amount ($\sim$0.04 g) of Sb shot (99.999% Alfa Aesar). The tube was heated to 900 °C for 80 min, and then the entire tube was quenched-cooled to room temperature. Scanning electron microscopy of unreacted and reacted microfibers showed an obvious change in the Mo-coating due to the reaction with ammonia and Sb, respectively (see inset of Fig. 1). Several bundles of Mo-coated fibers were reacted at the appropriate temperature and time period to get the sufficient amount of MoN and Mo$_3$Sb$_7$ for x-ray diffraction analysis. Well-ground powders of these fiber bundles samples were analyzed in a powder x-ray diffractometer equipped with a Cu $K\alpha$ ($\lambda = 1.54056$ Å) source. Data were collected from $2\theta = 20-80°$ with a scan interval of 0.02 deg/s at room temperature. The x-ray diffraction patterns verified the respective formation of hexagonal phase δ-MoN and Mo$_3$Sb$_7$ on the carbon fibers.

In addition, we formed planar films of each compound by first evaporating 60-nm thick films of Mo onto a sapphire substrates via e-beam vacuum deposition of arc-melted molybdenum buttons (99.999% Alfa Aesar). The resulting Mo films were then exposed to either ammonia gas or Sb vapor as per the recipes used to form the fiber coatings. Because the planar film synthesis did not involve carbon, it provided us with control samples from which we could determine the effects of possible carbon contamination from the fiber cores. The planar geometry, however, is not particularly suitable for critical current measurements. Reliable annular contacts were made by applying Epotek conductive epoxy directly onto the reacted fibers. Critical currents of 3–5 mm long fibers were measured in a four-probe geometry using a stan-
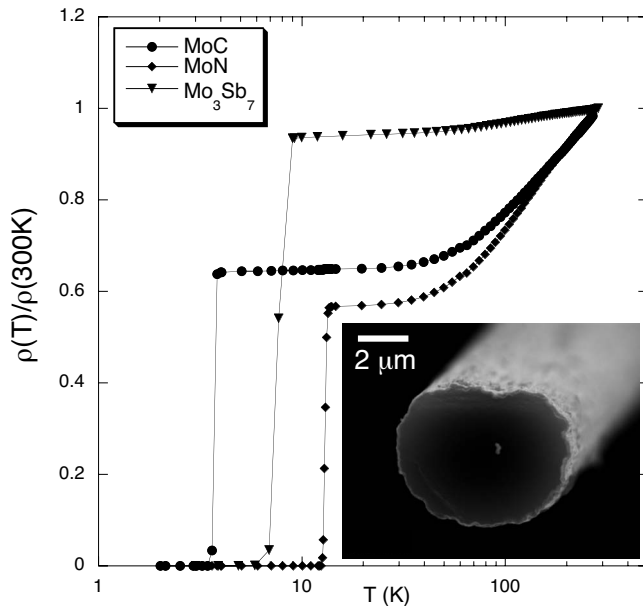
FIG. 1. Resistivity normalized by its room temperature value as a function of temperature for an unreacted Mo-coated carbon fiber, a MoN-coated fiber, and a Mo_3Sb_7-coated fiber. The unreacted fiber contained a significant fraction of Mo_2C formed during the manufacturing process. The 20 K resistivities of the MoN and Mo_3Sb_7 fibers were 10 and 60 $\mu\Omega$ cm, respectively. Inset: Scanning electron micrograph of the cross-sectional view of a MoN-coated carbon fiber.

FIG. 2. Normalized resistivities of a MoN film, a Mo_3Sb_7 film, and a Mo_3Sb_7 wire. The films were formed by reacting 60-nm-thick Mo films deposited on sapphire. The wire was formed by reacting a 0.07-mm diameter Mo wire in Sb vapor.

dard pulse technique. Currents were driven using pulse durations of 1–2 μs with a duty cycle of 1/1000, and the resulting voltages were measured via a boxcar integrator. Care was taken to ensure that the pulse width and duty cycle were low enough to avoid significant Joule heating at the contacts. The samples were cooled by vapor down to 1.8 K in magnetic fields up to 9 T via a Quantum Design PPMS.

III. RESULTS AND DISCUSSION

Shown in Fig. 1 is the temperature dependence of the resistivity of a pristine Mo-coated fiber, a MoN-coated fiber, and a Mo_3Sb_7-coated fiber. The resistivities have been normalized by their room temperature values. Note that each of these fibers underwent a superconducting transition at a temperature well above 1 K. The midpoint transition temperatures are T_c=3.7, 7.5, and 13.5 K for the MoC, Mo_3Sb_7, and the MoN fibers, respectively. The relatively high transition temperature of the pristine Mo-coated fiber is due to the fact that a portion of the molybdenum coating reacted with the carbon core to form Mo_2C, which itself has a $T_c \sim 4$ K.[4] The MoN fiber has a very sharp transition, with a 10–90% relative width $\Delta T_c/T_c \sim 0.05$. Its midpoint transition temperature is several Kelvins higher than that of polycrystalline cubic phase MoN ($B1$-MoN) films synthesized by pulsed laser deposition and comparable to pressure-annealed hexagonal phase (δ-MoN) films produced by magnetron sputtering.[12] Reactive vapor synthesis is an attractive alternative to these techniques for producing MoN because it allows one to independently control the Mo deposition parameters and,
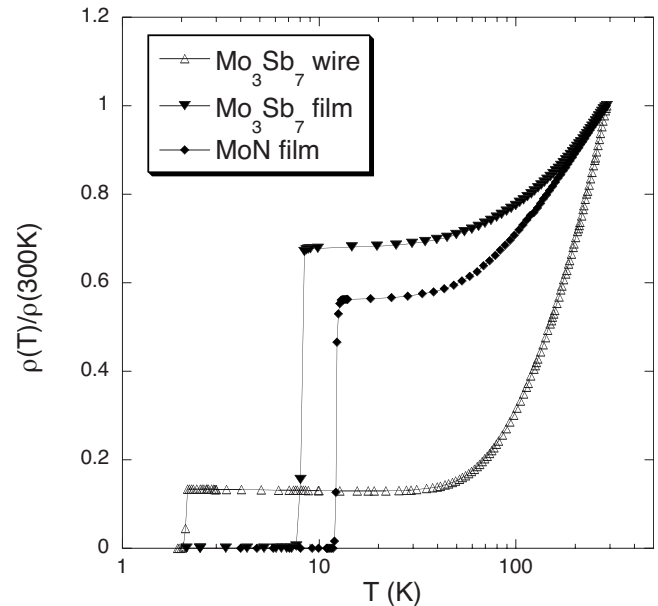
hence, the Mo film parameters, and it insures that the nitrogen rich phase is produced and not Mo_2N, for instance. Finally, we note that the transition temperature of the Mo_3Sb_7 fiber is almost a factor of four higher than the T_c=2.1 K, recently reported for Mo_3Sb_7 powders formed in solid state reactions.[13] As discussed below, we believe that this is a stress effect.

Carbon contamination is obviously a concern since the reactions take place on a carbon surface. In particular, carbon doping may play a role in the anomalously high T_c of the moly-antiminide fibers. Unfortunately, it is very difficult to quantify the extent of carbon contamination from x-ray analysis of the reacted fibers due to the large carbon background. To address this issue, we synthesized MoN and Mo_3Sb_7 films on sapphire substrates by exposing the 60-nm-thick Mo films to ammonia and antimony vapor, respectively, as per the above recipes. The molybdenum films were formed via e-beam deposition of Mo buttons held in tungsten boats, thus, there was no carbon involved in the process. Shown in Fig. 2 is the resistive superconducting transition of a MoN and a Mo_3Sb_7 film. Note that the transition temperature of each film is very close to what was obtained from their microfiber counterparts. This suggests that carbon contamination was not a significant factor in determining the T_c's of the fibers. Interestingly, we have also included in this figure the resistive transition of polycrystalline Mo_3Sb_7 wire formed by exposing a 0.07-mm diameter Mo wire to antimony vapor via the same recipe as used with the microfibers. Note that the wire has a T_c=2.1 K, as reported in bulk powder samples.[13] We believe that the enhanced T_c's observed in the microfibers and films are a stress effect. There is, in fact, a factor of four expansion in volume associated with the antimony reaction, which can, in principle, produce large internal stresses, especially in a thin film geometry. One pos-
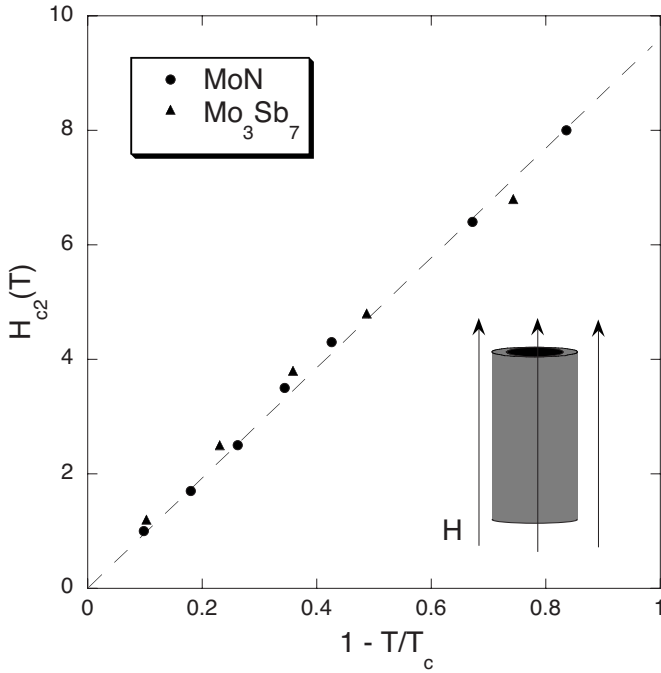
FIG. 3. Upper critical field of the MoN and Mo$_3$Sb$_7$ microfibers of Fig. 1 as a function of reduced temperature. The field was applied along the fiber axis as shown in the inset.
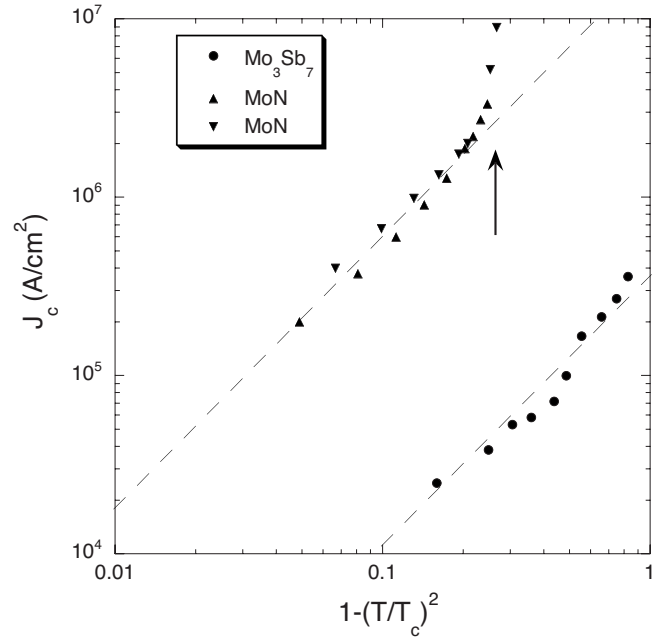

FIG. 4. Log–log plot of the critical current density as a function of reduced temperature. The triangles represent two different MoN microfibers. The arrow points to a sudden increase in the critical current density in the MoN fibers at $T \lesssim 10$ K. The dashed lines have slope 3/2 and are provided as a guide to the eye.

sible consequence of this is that there may be a molybdenum rich region near the carbon (or sapphire) interface. Substrate adhesion tends to inhibit film reactions that involve a large change in volume, and, in our case, the antimony may not be fully diffusing through the entire depth of the molybdenum coating. Alternatively, the superconducting phase itself may be more stable in a disordered and low dimensional geometry. It has been long known that thin, disordered films of some elements, such as Al and Be, for instance, have significantly higher transition temperatures than their bulk counterparts.[14,15] Although the origin of the T_c enhancement elemental films remains controversial, there may be an analogous and perhaps magnetically mediated effect in Mo$_3$Sb$_7$. There is speculation that the "bare" transition temperature of bulk Mo$_3$Sb$_7$ is near 8 K and that the relatively low observed transition temperature of 2.1 K is a consequence of strong spin fluctuations.[13] From this perspective, perhaps the spin-fluctuation amplitude in thin films of Mo$_3$Sb$_7$ is somewhat less than that of the bulk material, thus, resulting in a higher T_c.

In Fig. 3 we plot the upper critical field of a MoN and a Mo$_3$Sb$_7$ microfiber as a function of reduced temperature. The magnetic field was applied along the fiber axis. Note that the critical field behavior of the two systems is quite similar, with both data sets extrapolating to $H_{c2}(0) = 9.6$ T. This corresponds to a coherence length $\xi \approx 6$ nm. Since ξ is much less than either the MoN or Mo$_3$Sb$_7$ coatings, the superconducting layers are essentially in the infinite thickness limit. The H_{c2} has never been reported in a MoN film. However, the upper critical field of bulk polycrystalline Mo$_3$Sb$_7$ is 1.7 T. Not only is the critical field of the Mo$_3$Sb$_7$ microfiber significantly higher than that of powders, but also the *reduced* critical field $Hc2/T_c \sim 1.3$ T/K is much larger than

the 0.55 T/K of powder samples. Indeed, the former is near the Clogston–Chandrasekar limit.[10]

Critical current measurements in MoN and Mo$_3$Sb$_7$ microfibers were limited to temperatures above 5 K due to both the limitation of the electronics and the risk of damaging the samples. In Fig. 4 we present a log–log plot of the critical current density in zero magnetic field as a function of reduced temperature where we have defined J_c by the onset of voltage. The value of T_c, used to scale the data in Fig. 4, was determined by the onset of voltage at $J = 0.01 J_c$. Care was taken to reduce the pulse width and duty cycle to the point were no hysteresis was observed across the critical current threshold. The dashed line in Fig. 4 is the GL critical current behavior for a homogeneous order parameter,[10]

$$ J_c = \frac{H_c(T)}{3\sqrt{6}\pi\lambda(T)} \propto [1 - (T/T_c)^2]^{3/2}, \quad (1) $$

where H_c is the thermodynamic critical field and λ is the London penetration depth. λ has not been reported in either MoN or Mo$_3$Sb$_7$, therefore, we cannot compare the magnitude of the measured critical current densities with Eq. (1). However, the temperature dependence of J_c can be compared to Eq. (1) (see Fig. 4). Although both systems exhibited the expected 3/2 power law of Eq. (1) (dashed lines in Fig. 4), the critical current densities in the Mo$_3$Sb$_7$ microfibers were roughly an order of magnitude lower than those of the MoN fibers. Whether or not this is an intrinsic property of Mo$_3$Sb$_7$ remains unclear. Obviously, cracks and grain boundaries can undermine the maximum critical current density, but the fact that the data scales properly with reduced temperature suggests that the low critical current density of Mo$_3$Sb$_7$ is an

intrinsic property. In contrast, the extrapolated zero temperature critical current density of the MoN fibers was quite high, $J_c(0) \approx 5 \times 10^7$ A/cm^2, and, in fact, comparable to what we have previously reported for MgCNi$_3$ microfibers.[9] Interestingly, however, upon lowering the temperature below ~ 10 K, we observed a precipitous increase in the critical current density of the MoN microfibers (see arrow in Fig. 4). This abrupt deviation from the 3/2 scaling may be an effect associated with the pinning of self-flux. If flux motion is indeed limiting the critical current near T_c, then our data suggests that below 10 K, the flux rapidly becomes strongly pinned. At the onset of this pinning threshold the critical current density should begin to approach the pair-breaking limit. It is also possible, of course, that the system undergoes an unexpected phase transition.

IV. CONCLUSION

In conclusion, we report magnetotransport and critical current properties of MoN-coated and Mo$_3$Sb$_7$-coated carbon microfibers. The transition temperature of the MoN microfibers was comparable to that reported for MoN powders and films. The Mo$_3$Sb$_7$ microfibers, however, exhibited transition temperatures that were almost a factor of four higher than what is reported in powder samples. We believe that this is a stress effect and not a consequence of carbon doping. The critical current density of the MoN fibers was well described by Eq. (1) down to 10 K but increased much faster than $[1-(T/T_c)^2]^{3/2}$ at lower temperatures. In contrast, the critical current density of the Mo$_3$Sb$_7$ fibers exhibited the 3/2 scaling behavior across the entire temperature range, but the magnitude of the critical current density was anomalously low.

ACKNOWLEDGMENTS

[1] J. Muller, Rep. Prog. Phys. **43**, 641 (1980).

[2] E. Soignard, P. F. McMillan, T. D. Chaplin, S. M. Farag, C. L. Bull, M. S. Somayazulu, and K. Leinenweber, Phys. Rev. B **68**, 132101 (2003).

[3] C. L. Bull, P. F. McMillan, E. Soignard, and K. Leinenweber, J. Solid State Chem. **177**, 1488 (2004).

[4] B. T. Matthias and J. K. Hulm, Phys. Rev. **87**, 799 (1952).

[5] D. A. Papaconstantopoulos, W. E. Pickett, B. M. Klein, and L. L. Boyer, Phys. Rev. B **31**, 752 (1985).

[6] D. A. Papaconstantopoulos and W. E. Pickett, Phys. Rev. B **31**, 7093 (1985).

[7] Z. Bukowski, D. Badurski, J. Stepien-Damm, and R. Troc, Solid State Commun. **123**, 283 (2002).

[8] C. Candolfi, B. Lenoir, A. Dauscher, C. Bellouard, J. Hejtmánek, E. Šantavá, and J. Tobola, Phys. Rev. Lett. **99**, 037006 (2007).

[9] T. He, Q. Huang, A. P. Ramirez, Y. Wang, K. A. Regan, N. Rogado, M. A. Hayward, M. K. Haas, J. S. Slusky, K. Inumara, H. W. Zandbergen, N. P. Ong, and R. J. Cava, Nature (London) **411**, 54 (2001).

[10] D. P. Young, M. Moldovan, and P. W. Adams, Phys. Rev. B **70**, 064508 (2004).

[11] M. Tinkam, *Introduction to Superconductivity* (McGraw-Hill, New York, 1996).

[12] J. W. Composites, LC, 420 South 500 West, Salt Lake City, UT 84101.

[13] H. Ihara, M. Hirabayashi, K. Senzaki, Y. Kimura, and H. Kezuka, Phys. Rev. B **32**, 1816 (1985).

[14] P. W. Adams, P. Herron, and E. I. Meletis, Phys. Rev. B **58**, R2952 (1998).

[15] Wenhao Wu and P. W. Adams, Phys. Rev. Lett. **73**, 1412 (1994).