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Superconducting and magnetotransport properties of $ZnNNi_3$ microfibers and films

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We present the superconducting and critical current properties of $ZnNNi_3$ in the form of annularly coated carbon microfibers and thin films. The fibers were prepared by heating 6–8 μm diameter commercially available Ni-coated carbon fibers with Zn powder in a flowing stream of NH_3 gas at 650 °C. The fibers had a T_c=3.75 K, which was slightly higher than that of the polycrystalline powder and an upper critical field, $H_{c2}(0)=0.92$ T. Near the transition temperature T_c, the critical current density J_c was well described by the Ginzburg-Landau power-law form $[1-(T/T_c)^2]^{3/2}$. The extrapolation produces $J_c(0)\cong 1.45\times 10^6$ A/cm^2. An axial magnetic field produces an exponential decrease in the critical current density. Planar $ZnNNi_3$ films were formed on sapphire substrates by exposing thin Ni films to a similar heat treatment as the fibers. Hall measurements on the films in the normal state revealed a carrier density, $n=-1.46\times 10^{23}$ cm^{-3}.

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I. INTRODUCTION

In recent years a broad and significant research effort has emerged that aims at identifying and characterizing relatively low-T_c superconductors that are exotic in their normal state properties and/or order parameter symmetries. Two important examples of such systems are the strong spin-fluctuating superconductor Mo_3Sb_7 (Ref. 1) and the nonoxide perovskite superconductor $MgCNi_3$.[2] The nature of the superconducting ground state in these compounds remains controversial,[3–5] owing to the fact that they are believed to be close to a ferromagnetic instability. Extensive searches have been made for other nonoxide perovskite superconductors, with particular interest in Ni-based compounds, such as (Cd, Zn, Al, In, Ga) C_yNi_3.[6–11] Among them, only $CdCNi_3$ was found to exhibit a superconducting transition. Recently, however, a carbon-free 3 K perovskite superconductor, $ZnNNi_3$, has been discovered.[12] It is the first nitrogen-containing superconducting material in the Ni-based perovskite series. ZnN_yNi_3 forms in a cubic structure with space group $Pm3m$. The lattice parameter and nitrogen content (y) were determined to be 3.756 Å and 1.012, respectively.[12] The superconducting transition temperature (T_c) and critical fields (H_{c1} and H_{c2}) were determined from resistivity and magnetization measurements on powder samples of $ZnNNi_3$ prepared by reacting pressed pellets of $Zn_{1.05}Ni_3$ in NH_3 gas. Shein *et al.*[13] believed that the origin of the superconducting state in $ZnNNi_3$ can be attributed to the effect of nitrogen vacancies on the electronic spectra of nitrogen-deficient $ZnN_{1-x}Ni_3$.

In this Brief Report we present magnetotransport studies of $ZnNNi_3$ synthesized in the form of thin wires, annular fibers, and thin films. The transport critical current density of annular $ZnNNi_3$ microfibers has been measured as a function of temperature and field. Intermetallic superconductors with high transport critical current density (J_c) have potential technological applications. The synthesis of this material in the form of a very thin annular region on the surface of a carbon fiber is ideal for measuring J_c since the small wires have a fairly large normal-state resistance. We show that the scaling behavior of J_c near the transition temperature T_c is well described by a Ginzburg-Landau (GL) form. In addition, we show that the critical current is exponentially suppressed by an axial magnetic field over the entire field range from 0 to 3 kG with no significant hysteresis. This behavior suggests that superconducting vortex pinning is weak in polycrystalline $ZnNNi_3$.

II. SAMPLE PREPARATION

Several pieces of 2-cm-long, 50 μm diameter Ni wire obtained from Alfa Aesar were first heated with stoichiometric amounts of Zn powder in an evacuated quartz tube at 650 °C for 2 h. The Zn-reacted wires were then heated in a 1 atm stream of ammonia gas (NH_3) at 650 °C for 2 h to form $ZnNNi_3$ wires. Annular $ZnNNi_3$ films were formed on Ni-coated carbon fibers obtained from Novamet Specialty Products Corporation under the product name Incofiber 12K20.[14] The commercial fibers consist of a 6–8 μm diameter solid carbon core onto which an 80-nm-thick film of Ni has been deposited via a proprietary chemical vapor deposition process. We formed $ZnNNi_3$ by heating the Ni-coated carbon fibers in a 1 atm stream of ammonia gas (NH_3) with 0.002 g of Zn at 650 °C. Samples with the best superconducting properties were obtained by heating the quartz tube from 0 to 650 °C in 25 min and then quench cooling to room temperature. Scanning electron micrographs of reacted microfibers showed an obvious change in the Ni coating due to the reaction with ammonia and Zn (see insets of Fig. 3). A factor of 2 expansion in the volume of the coating is clearly evident in the micrographs. In addition, we formed planar films of $ZnNNi_3$ by first evaporating 100- and 45-nm-thick films of Ni onto sapphire substrates via e-beam vacuum deposition of arc-melted Ni buttons (99.999% Alfa Aesar). The resulting Ni films were then exposed to ammonia gas and Zn 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. Reliable electrical contacts were formed by attaching 2-mil diameter Pt wires with Epotek conductive epoxy directly onto the reacted fibers and thin films. Critical currents of 3–5-mm-long $ZnNNi_3$-coated carbon fibers were

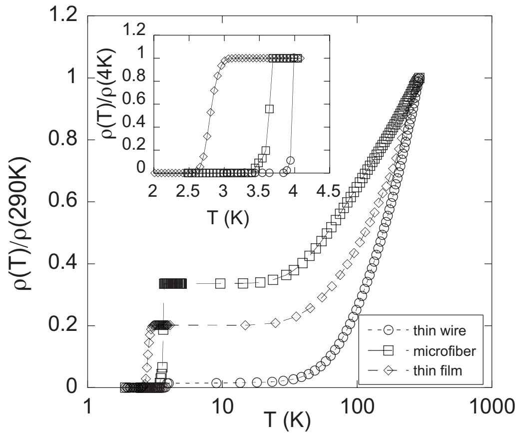

FIG. 1. Semilogarithmic plot of normalized resistivities of a wire, a microfiber, and a thin film of $ZnNNi_3$. The inset shows the superconducting transitions at low temperature.

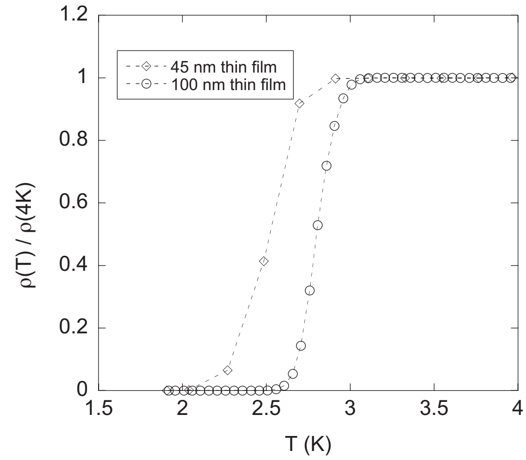

FIG. 2. Resistive transitions for $ZnNNi_3$ thin films with thicknesses of 45 and 100 nm.

measured in a four-probe geometry using a standard pulsed 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 physical property measurement system.

III. RESULTS AND DISCUSSION

The temperature dependence of the resistivity of a $ZnNNi_3$ wire, a $ZnNNi_3$-coated fiber, and a 100-nm-thick $ZnNNi_3$ thin film is shown in Fig. 1. The resistivities have been normalized by their room temperature values. As shown in the inset of Fig. 1, each of these samples underwent a superconducting transition. The midpoint transition temperatures are T_c=2.75, 3.65, and 3.8 K for the thin film, the microfiber, and the wire, respectively. The fiber and the wire both have very sharp transitions. Their transition temperatures are, in fact, higher than the onset T_c=3 K, recently reported for powder samples synthesized by heating pressed pellets of $ZnNi_3$ in a stream of NH_3 gas.[12] For the $ZnNNi_3$-coated microfiber, carbon contamination is obviously a concern since the reactions take place on a carbon surface. Note that the transition temperature of the wire is only slightly higher than what was obtained from its microfiber counterpart. This suggests that carbon contamination was not a major factor in determining the superconducting properties of the microfibers. The residual resistivity ratios ($\rho_{290\ K}/\rho_{4\ K}$) are 4.97, 2.98, and 69.26 for film, fiber, and wire, respectively. As shown in Fig. 2, the superconducting transition temperature of the planar films decreases with decreasing film thickness. This trend is not unusual in intermetallic systems, and we expect the thinner films to be more disordered (less crystalline). A similar result was observed in thin films of $MgCNi_3$, also formed via a vapor reaction process.[15]

The upper critical field, H_{c2}, of $ZnNNi_3$ microfibers was determined from the resistivity (ρ) data at various temperatures. The magnetic field was applied along the fiber axis. The upper critical field, defined as the midpoint of the transition, is plotted as a function of temperature in Fig. 3. The upper critical field at T=0 [$\mu_0 H_{c2}(0)$] can be estimated by the Werthamer-Helfand-Hohenberg (WHH) formula for a BCS superconductor with weak coupling,[16]

$$\mu_0 H_{c2}(T) = -0.693(dH_{c2}/dT_c)T_c, \tag{1}$$

where the slope dH_{c2}/dT_c was estimated to be -0.38 T/K. For T_c=3.5 K, $\mu_0 H_{c2}(0)$ was found to be 0.92 T. GL theory provides an alternative estimate for the upper critical field, where $\mu_0 H_{c2}(0)$ can be determined from the simple empirical formula[17]

$$H_{c2}(T) = H_{c2}(0)(1-t^2), \tag{2}$$

where $t=T/T_c$ and $H_{c2}(0)$ is the upper critical field extrapolated to 0 K. The solid line in Fig. 3 represents the best fit of the experimental data to Eq. (2). The extrapolation yielded $\mu_0 H_{c2}(0)$=0.86 T as shown in the figure—a value slightly

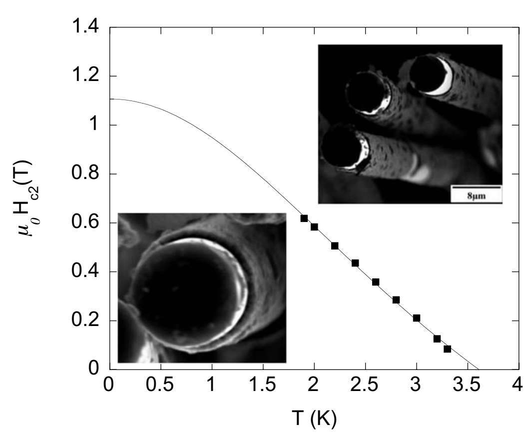

FIG. 3. Upper critical field of a $ZnNNi_3$-coated carbon microfiber as a function of temperature. The field was applied along the fiber axis. The solid line is a fit to GL theory as described in the text. Inset: scanning electron micrograph of the reacted fibers, clearly showing the reacted surface layer.

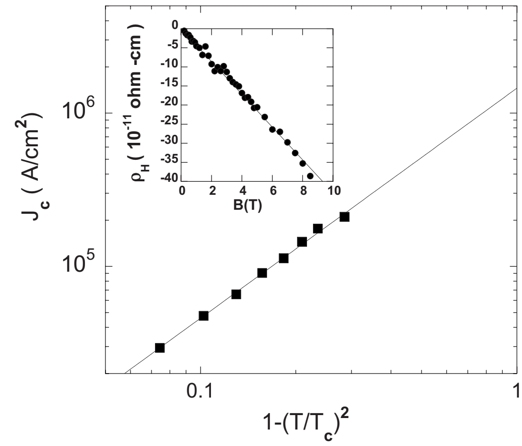

FIG. 4. Log-log plot of the critical current density as a function of reduced temperature. The solid line has a slope of 3/2. Inset: Hall voltage of a 100 nm $ZnNNi_3$ film measured at 5 K. The dashed line is a linear least-squares fit to the data. The low-temperature data correspond to a carrier density of $n = -1.46\times 10^{23}/\mathrm{cm}^3$.

smaller than the WHH estimate. The corresponding superconducting coherence length, $\xi(0) = 191.27$ Å, was calculated using the Ginzburg-Landau formula for an isotropic three-dimensional superconductor $H_{c2}(0) = \Phi_0/2\pi\xi(0)^2$, where $\Phi_0 = 2.0678\times 10^9$ Oe Å^2 is a flux quantum.[17] The reported upper critical field and coherence length of powder $ZnNNi_3$ are 0.96 T and 185 Å, respectively.[12] Thus, the film thickness is larger than $\xi(0)$.

The higher transition temperature observed in our samples is most likely due to the synthesis technique. In both cases (films and fibers) a thin Ni layer is exposed to an abundance of Zn vapor and NH_3 gas. The stoichiometry is essentially self-selecting, as the reaction takes place until the Ni layer is completely reacted. Additionally, samples formed in these geometries are most certainly under some strain which may contribute to the enhancement of the superconducting transition temperature. We have already observed an enhancement in the superconducting properties of Mo_3Sb_7 synthesized in the form of wires, microfibers, and thin films.[18]

In-plane Hall measurements were made on the 100-nm-thick film of $ZnNNi_3$ in the normal state. In the inset of Fig. 4 we show the Hall resistivity as a function of magnetic field at 5 K. The solid line is a linear least-squares fit to the data. The slope of the line is proportional to the Hall coefficient, $R_H = 1/en$, where n is the effective carrier density. The data clearly show that the film has electronlike carriers, with a carrier density, $n = -1.46\times 10^{23}$ cm^{-3}, which is approximately ten times that reported in thin films of $MgCNi_3$.[15]

Critical current measurements on $ZnNNi_3$ microfibers were limited to temperatures above 1.9 K due to both the limitation of the electronics and the risk of damaging the samples. In Fig. 5 we present a log-log plot of the critical current density in zero magnetic field as a function of the 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 where no hysteresis was observed across the critical current threshold.

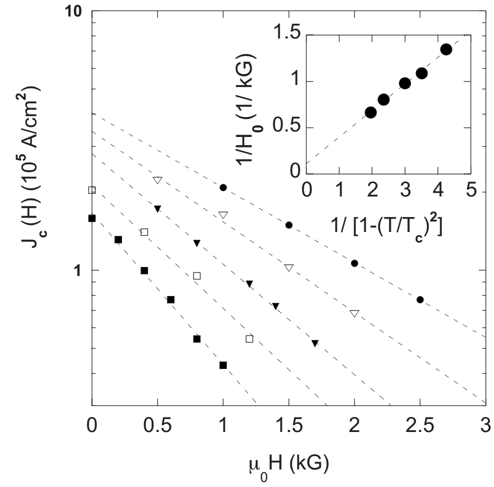

FIG. 5. Semilogarithmic plot of the magnetic field dependence of the critical current density at several temperatures: 3, 2.9, 2.8, 2.6, and 2.4 K from left to right. The field was applied longitudinally to the fiber. The dashed lines represent exponential fits to the data from which a characteristic decay field H_0 is extracted. Inset: inverse of characteristic field as a function of inverse of reduced temperature. The dashed line is provided as a guide for the eyes.

The solid line in Fig. 4 represents the GL critical current scaling behavior for a superconductor with a homogeneous order parameter,[19,20]

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

where H_c is the thermodynamic critical field and λ is the London penetration depth. The solid line in Fig. 4 has slope 3/2 as predicted by Eq. (3). The extrapolated zero-temperature critical current density was $J_c(0) = 1.45\times 10^6$ A/cm^2, which is comparable to what we have previously reported for Mo_3Sb_7 microfibers but lower by 1 order of magnitude than that for $MgCNi_3$ and MoN microfibers.[18,20] Obviously, cracks and grain boundaries can undermine the maximum critical current density, but the fact that the data scale properly with reduced temperature suggests that the low critical current density of $ZnNNi_3$ is an intrinsic property. Furthermore, using the values for the penetration depth and critical field from Ref. 12, the value for J_c obtained from Eq. (3) is 5.7×10^6 A/cm^2, which is comparable to our extrapolated value.

The behavior of the critical current density as a function of magnetic field at several temperatures is shown in Fig. 5. The magnetic field was applied axially to the fibers. It is interesting to note that the exponential decay of J_c exists over the entire field range. Generally, very few systems show an exponential dependence over a wide range of fields. The dashed lines in the main panel of the figure are exponential fits to the data with equation

$$J_c(H,T) = J_c(T)\exp[-(H/H_0)], \qquad (4)$$

where H_0 is a characteristic field (see inset of Fig. 5). Interestingly, virtually no hysteresis in either field or current was observed during the course of these measurements, suggesting that flux pinning was not significant. This behavior is similar to what we obtained for $MgCNi_3$ microfibers.[20] This indicates the formation of a uniform coating of $ZnNNi_3$ in the annular region of the microfibers. In the inset of Fig. 5, the characteristic field is plotted as a function of temperature. The dashed line is a linear fit to the data.

IV. CONCLUSION

In conclusion, we successfully synthesized $ZnNNi_3$ in the form of thin films and annular coatings on the surface of carbon microfibers and analyzed the magnetotransport and critical current properties. The critical transition temperature of the $ZnNNi_3$-coated microfibers is slightly higher than that reported for polycrystalline $ZnNNi_3$. The temperature and field dependence of the critical current density are well described by $J_c(T,H)=J_c(0)[1-(T/T_c)^2]^{3/2}\exp[-(H/H_0)]$ over the entire range of temperature and field. The magnitude of the critical current density is lower than that reported for isostructural $MgCNi_3$, and the scaling behavior suggests that this is an intrinsic property of $ZnNNi_3$.[20] The $ZnNNi_3$ film has electronlike carriers with a carrier density higher than that reported for $MgCNi_3$.[15]

The results of our previous studies of $MgCNi_3$, MoN, and Mo_3Sb_7 and the present research on $ZnNNi_3$ in the form of wires, thin coatings on carbon microfibers, and as thin films have established the synthetic method described above as a very reliable synthesis technique for intermetallic superconductors.[18,20] Also, this deposition method is ideal for critical current studies, where it tends to produce quite uniform coatings with excellent adhesion.

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