Bi nanowires: Magnetism and the semimetal-to-semiconductor transition

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Abstract. Cantilever magnetometry experiments were performed on arrays of Bi nanowires of various diameters both on the semimetal and semiconductor side of the semimetal-to-semiconductor transition (SMSC) that is predicted to occur for diameters of approximately 50 nm. Our 270 nm nanowire samples, which are on the semimetal side of the SMSC transition, exhibit strong dHvA oscillations that can be interpreted by considering crystalline orientation and size effects and a large magnetization. Arrays of wires with diameters near or below the SMSC (60 and 36 nm) have dramatically reduced magnetizations per volume, and do not exhibit dHvA oscillations, consistent with a reduction in free carriers due to the SMSC.

1. Introduction
The magnetic properties of low dimensional systems have been actively investigated [1], especially in nanostructures such as quantum dots, rings, and films, which are of interest because of their potential for electronic device applications. In spite of the new fundamental physics embodied by systems of nanowires - systems with charge carriers confined in two of three dimensions - there have been few experimental investigations of the magnetic properties, with the exception of carbon nanotubes [2].

Bismuth is an ideal material for studying the properties of quantum wires due to its high carrier mobility and small electron effective mass [3]. Moreover, Bi nanowire arrays are well-suited to such studies, as the sample mass is fairly large and the wires have preferential crystalline orientation along the wire axis. However, most investigations of Bi nanowire arrays focus on the structural properties, electronic transport properties [4 - 6] or optical properties [7] of the nanowires. To our knowledge, there have been no studies of the magnetic properties of Bi nanowires.

Crystalline bulk Bi is a diamagnetic semimetal, with a Fermi surface (FS) that consists of three electron pockets at the L point and a T-point hole pocket [8,9]. The effective band overlap energy, $E_0$, and the Fermi energy, $E_F$, are 37 and 26 meV respectively. These result in electron and hole densities of $n_e = p_h = 3 \times 10^{17} / \text{cm}^3$ at 2 K. Quantum confinement effects decrease the overlap and promote a semimetal-semiconductor (SMSC) transition for $d \sim 2\hbar/(2m^*E_0)^{1/2} \sim 50$ nm ($m^*$ is the cyclotron mass transverse to the wire axis). Clearly, the SMSC transition involves a depopulation of the electron and hole bands.

One aim of our experiments is to follow the carrier densities over a range of wire diameters using the magnetization as a probe. Typically measurements of the magnetization require large samples, which can be a problem in the study of nanowires. As noted above, our sample mass is macroscopic as...
Bi nanowires can be fabricated in massively parallel arrays. For example, the 36 nm nanowire array studied here contains $10^9$ wires in parallel per $\text{mm}^2$, with a total sample mass of 0.5 mg in a volume of 0.1 $\text{mm}^3$, roughly. Additionally, for enhanced sensitivity our measurements are carried out utilizing a cantilever magnetometer.

2. Experimental
We have studied arrays with $36 \pm 3$, $60 \pm 14$ and $270 \pm 40$ nm diameter nanowires (where the statistical error is determined from measurements done on scanning electron microscope images). Molten Bi is pressure injected into porous alumina (PAAO) templates with a hexagonal array of nanochannels [4]. Individual wires are composed of highly oriented crystalline grains [5], with more than 90% of the wires are oriented along the trigonal axis according to XRD measurements [7]. To compare magnetization per volume of Bi, the respective volume fractions of the PAAO and Bi were estimated using SEM images. The images showed Bi volume fractions of $0.34 \pm 0.12$, $0.12 \pm 0.06$, and $37 \pm 12\%$ for the 36, 60 and 270 nm nanowire arrays respectively.

We performed the magnetometry measurements with a Si cantilever mounted in a $^3\text{He}$ refrigerator with a 9 Tesla superconducting magnet. Deflection is measured from the capacitance between the paddle and a fixed gold plate. Measurements of the torque response were taken at field center in two orientations where the wire (trigonal) axis was at angles of 13 and 81 degrees with field. The cantilever was oriented with the wires parallel to the surface normal of the cantilever. The shape anisotropy of the wires causes the magnetization to lie along the wire axis, and the field-induced torque will tend to align the nanowires with the applied field. Assuming small displacements of the cantilever, the sample magnetization per volume is proportional to the fractional change of the capacitance in field $H$

$$M \propto \frac{C(H) - C(0)}{C(0)HV_{Bi}} = \frac{\Delta C(H)}{C(0)HV_{Bi}}$$

where $V_{Bi}$ is the calculated volume of Bi for a given nanowire array.

We measured magnetic field response of the silicon cantilever with empty substrates, and this response was subtracted from data taken with samples mounted on the cantilever. Table 1 shows the maximum signal (calculated from Eq. 1) from the Bi in the samples as a percent of the total maximum signal. Temperatures are shown in Figures 1 and 3 and the signals were compared over the entire magnetic field range from 0 to 9 T. It is immediately evident that for wire diameters near or below the SMSC transition the overall size of the magnetization is dramatically reduced compared to that for the 270 nm nanowire array, with the magnetic signal becoming comparable to that of the cantilever and template material. Note that the mass of Bi in the 60 nm sample is actually greater than that for the 270 nm sample.

| Mass (mg) | 36 nm/13° | 60 nm /13° | 270 nm /13° | 36 nm /81° | 60 nm /81° | 270 nm /81° |
|----------|-----------|-----------|------------|-----------|-----------|------------|
| Bi signal % of total | 13% | 47% | 96% | 47% | 75% | 98% |

3. Results
The magnetic response for the three wire diameters at a wire orientation of 13 degrees with respect to the field direction is shown in Figure 1, and the derivative of this magnetization with inverse field for the 270 nm array is shown in Figure 2. Positive values in Figure 1 correspond to a paramagnetic response. After peaking at around 0.5 T the signal of the 270 nm array continues at high field with a
negative slope. The 36 and 60 nm arrays show virtually no magnetic response after sharp peaks at very low fields. The magnetization curves are essentially independent of temperature below 2 K.

Figure 1. Magnetization per volume of Bi versus field for various wire diameters at an angle of 13° with field.

Figure 2. Derivative of magnetization with inverse field for 270 nm wires with an orientation of 13°.

Only the 270 nm array shows significant oscillations in the magnetization. Two types of oscillations can be seen in Figure 2; large amplitude slower oscillations, and small amplitude fast oscillations. Blank PAAO templates were measured and showed the second type of oscillations leading to the conclusion that it is not intrinsic to the Bi. The (large amplitude) slow oscillations, which we attribute to dHvA, have a period of 0.27 ± 0.03 T⁻¹, which is shown in Figure 4 by plotting the inverse field locations of the maxima and minima of each oscillation on an integer scale. The peak in magnetization of the 270 nm array around 0.5 T does not fit the periodicity of the other oscillations in inverse field and so is not associated with dHvA.

Quantum confinement should begin to play a role as the diameter of the wire is reduced below the cyclotron orbit of the carriers. When this happens, the band gap is increased and there are no carriers left in unfilled states. This means the outermost Landau level is always full and the magnetization will no longer oscillate with field. The lack of observable dHvA oscillations signals the SMSC transition.

4. Discussion

The strength of the dHvA oscillatory magnetic signal of 270 nm wire arrays is comparable with that of bulk Bi. At an orientation of 13 degrees between the field and the trigonal direction the periods for electron pockets lie between 0.1 T⁻¹ and 0.25 T⁻¹. Holes have a period of 0.16 T⁻¹ [8, 9]. Our measurement of 0.27 T⁻¹ identifies the carriers as electrons. At 81 degrees the value of electron periods ranges from 0.09 T⁻¹ to 0.7 T⁻¹ while the hole period is 0.055 T⁻¹. The observed period of 0.49 T⁻¹ again agrees electron carriers. This result also agrees with previous dHvA measurements done on Bi microwires [10]. The smaller diameter nanowires do not exhibit dHvA oscillations, suggesting that the strong reduction in carrier density near the SMSC transition both reduces the magnitude of the magnetization and the dHvA signal.
The mixed paramagnetic-diamagnetic behavior warrants further study. The magnetization of bulk Bi is roughly linear with magnetic field and negative (diamagnetic), and 50 μm Bi microwire arrays exhibit a similar behavior [10]. In contrast, the magnetization of nanowires, for which the measured contribution from the PAAO templates has been subtracted, exhibit strikingly different behaviour, with a maximum occurring at field values near 1 T. The maxima is suggestive of the ‘Chambers peak’ phenomenon observed in the magnetic field dependence of the electrical resistance, which occurs due to a mobility change as the cyclotron orbit becomes comparable to the nanowire diameter, with the crossover field is given by $B_c = \frac{h k_F}{\pi e d}$. Here $k_F$ is the carrier Fermi wavevector and $d$ is the nanowire diameter [6]. In Bi nanowires, Chamber’s effects are signalled by an increase of electron mobility, $B > B_c$. $B_c \sim 1$ T for 270 nm nanowires, while for the 60 nm nanowires, $B_c \sim 0.4$ T. This is related to the SMSC; in 60 nm nanowires the carrier concentration is smaller than in the bulk and therefore $k_F$ is smaller. Similar effects on $k_F$ were studied by Heremans et al [11]. Therefore, our preliminary experiments may show quantum confinement, necessitating more systematic measurements on samples over the diameter range 60 nm < $d$ < 500 nm. Finally, we also plan to study the low-T temperature-dependence of the magnetization of nanowire arrays ($d < 36$ nm) to determine if there is a diverging susceptibility, as predicted for a Luttinger liquid; in such very small wires surface carriers may compensate for the lack of ‘bulklike’ carrier states below the SMSC [5].

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