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1991 J. Phys.: Condens. Matter 3 7153

(http://iopscience.iop.org/0953-8984/3/37/007)

J. Phys.: Condens. Matter 3 (1991) 7153–7160. Printed in the UK

Electrical transport in bismuth whiskers at millikelvin temperatures

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Received 8 May 1991

Abstract. We have investigated the electrical conductivity of 1–5 μm thick bismuth whiskers at temperatures down to 20 mK, and in parallel and perpendicular magnetic fields up to 9 T. In parallel fields we searched for, but found no evidence of, triplet-paired multivalley superconductivity. In perpendicular fields $H > 0.5$ T we observe a small temperature-dependent contribution to the resistivity on top of the large classical magnetoresistance; comparison with predicted electron–electron interaction effects suggests that the dominant conduction path is a two-dimensional surface layer.

1. Introduction

In recent years, there has been considerable interest in the electronic transport properties of disordered systems, particularly in reduced dimensions [1, 2]. Quantum mechanical corrections to the conductivity due to weak localization and interaction effects have been investigated in detail, and good agreement between theory and experiment has emerged from these studies.

In the case of clean or very weakly disordered systems, the nature and importance of such corrections to the conductivity are less clear. In the limit of no disorder, when the background charge is uniformly distributed, low-electron-density systems (e.g. semimetals and semiconductors) have been predicted to exhibit such collective phenomena as spin density waves, charge density waves and Wigner crystallization [3]. In addition, there are recent predictions that these systems should exhibit a novel form of superconductivity in which a large magnetic field compresses the electron wave function and allows short-range attractive interactions to dominate over the long-range Coulomb repulsion, thereby allowing a multivalley, spin triplet superconducting state to form [4]. This state would exhibit the usual triangular lattice of flux tubes, but with the interesting property that the order parameter is enhanced, rather than suppressed, inside the flux tubes.

The experimental observation of such a novel superconductor may be extremely difficult, however, because of the dramatic effect even a small number of impurities can have on the conductivity of three-dimensional systems in high magnetic fields. 'Magnetic freeze-out' is a well studied phenomenon in which the electron

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0953-8984/91/377153+08$03.50

wave functions are compressed and the carriers become localized on impurities [5]. More recently, Hopkins *et al* [6] have studied a similar effect in doped germanium samples which they termed 'magnetic-field-induced localization' because although the resistance of the samples increased dramatically with applied field, the carrier concentration—as determined from the Hall coefficient—changed by a comparatively small amount.

Motivated by these considerations, we have studied electrical transport in the semimetal bismuth at temperatures down to about 10 mK and in magnetic fields up to 9 T. Bismuth is an attractive material for transport studies because of its low carrier concentration ($n_e \simeq 3 \times 10^{17}$ cm^{-3}), and because it already exhibits conventional superconductivity (in amorphous thin films where the carrier concentration is several orders of magnitude higher [7]) and thus may have a sufficiently strong electron–phonon interaction to exhibit the predicted high-field superconductivity. We chose to work with whiskers, both because they are single crystals of high chemical purity [8], and because there is some interest in them owing to the results of Overcash *et al* [9] who observed continued metallic behaviour in Bi whiskers down to 0.3 K.

2. Experimental set-up

We grew our whiskers from a starting material of 99.999% pure Bi using the 'squeeze' technique [10] in vacuum at 200 °C. The samples used in the experiment were made by breaking off suitably straight sections of whisker with a pair of fine tweezers, and placing them on coin silver blocks covered with 12 μm thick Kapton [11] film. We then used silver paint to make four contacts between the whisker and a set of copper pads which had previously been evaporated onto the Kapton film. To protect the whiskers from oxidation and accidental damage, and to supply additional thermal contact, we covered the whole assembly with a small drop of GE 7031 varnish.

Table 1. Diameter, room temperature resistivity, and residual resistivity ratio for the Bi whiskers used in the experiments.

Sample	Diameter (μm)	ρ_{300} ($\mu\Omega$ cm)	RRR
2	5.20(10)	270(10)	5.9
4	1.29(08)	400(50)	2.0
8	2.00(06)	820(50)	1.0
9	1.70(10)	480(50)	1.9

Examination of the whiskers with an optical microscope showed that they were not circular in cross section, but appeared to be faceted. This examination also revealed that the surface of the whiskers was somewhat speckled and rough on a length scale of ~0.1–0.5 μm. We used a calibrated photographic system attached to the microscope to measure the length and diameter of the whiskers. From those results and the measurement of the sample resistance, we obtained values for the room temperature resistivities ρ_{300} of the whiskers (under the assumption of a circular cross-section). These values, along with the residual resistivity ratios (RRR $\equiv \rho_{300}/\rho_{4.2}$), are summarized in table 1 for the four samples reported on in this paper. All of the measured resistivities are somewhat larger than the accepted value $\rho_{300} =$

107 $\mu\Omega$ cm, although the values for the RRR are consistent with previously reported experiments on Bi whiskers [9]. Since the room temperature bulk mean free path (~3 μm) is already on the order of the whisker diameter, some of this excess resistivity may be due to surface scattering, rather than scattering from defects. In addition, the fact that sample 2 has both a large diameter and a reasonably large RRR suggests that approximating the whiskers as circular may over estimate their effective cross-section by as much as a factor of 2.

The samples were mounted on a dilution refrigerator equipped with a 9 T magnet in such a way that the long axis of the whisker was either parallel or perpendicular to the applied field. We used a conventional auto-balancing AC resistance bridge to make four-wire measurements on the sample as functions of magnetic field and temperature. The bridge excitation was adjusted so that under typical conditions the power dissipated in the sample was of the order of 0.05 pW. In order to eliminate electrical interference which would also heat the sample, our bridge wiring included π-type 1 MHz low-pass filters in a shielded junction box at the head of the cryostat, and resistors in the sample leads at low temperatures. We determined the sample temperature from resistive thermometers calibrated against the melting pressure of ^{3}He.

3. Zero-field results

Figure 1 shows the sample resistance as a function of temperature in the absence of a magnetic field for all four whiskers. The vertical axis is expressed as percentage change to allow all four whiskers to be shown on the same scale. It is interesting to compare these results to those of Overcash *et al* [9] who measured the resistance of Bi and Bi–6 at.% Sb whiskers down to 300 mK. They found that the whiskers were always metallic. That is, as they lowered the temperature, the whisker resistance continued to decrease with a temperature dependence $\Delta R/R \propto T^{1.5}$. This behaviour has been interpreted as a competition between anti-localization (localization with strong spin–orbit scattering) and interaction effects [2]. In contrast, we find that, while the resistance of our whiskers decreases with temperature above 1 K, at low temperatures they cross over to the behaviour illustrated in figure 1. Except for sample 2, all of the whiskers show a slight *increase* in resistance at the lowest temperatures. This increase in $\Delta R/R$ is of the same order as the decrease below 1 K observed in [9] whereas it is clearly smaller than the increase ($\Delta R/R \sim 2\%$) seen over the same temperature range in sputter-deposited polycrystalline wires [12].

In systems with strong spin–orbit scattering, the corrections to the conductivity due to weak localization (in zero field) and electron–electron interactions have the same temperature dependence, but opposite sign. If the ratio of L_φ, the phase breaking length, to the thermal length, $L_T = \sqrt{\hbar D/k_B T}$ where D is the diffusion constant, is approximately 10:1, these two effects will largely cancel, as has been proposed [2] to explain the data of [9]. Because our whiskers show a resistance increase, rather than decrease, at low temperatures, the ratio of L_φ to L_T must be smaller in our samples, i.e. interaction effects must dominate. We believe that our whiskers are of substantially the same quality as those of [9], so our values for D (and therefore L_T) should not be very different. Our observed resistance increase must therefore be due to a reduction in L_φ. While magnetic impurities in the bulk of the whiskers would be an obvious mechanism for this reduction, they would not explain why the resistance

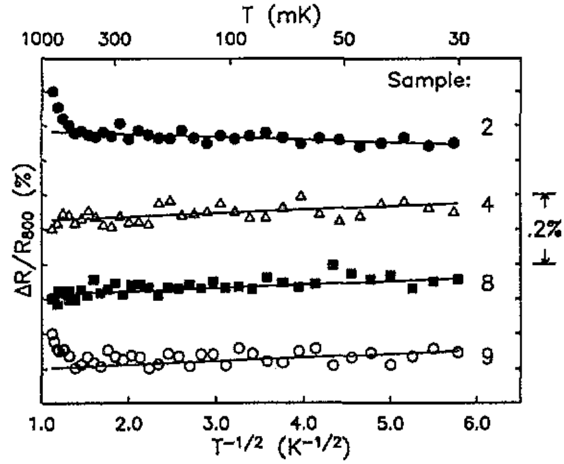

Figure 1. Percentage change in sample resistance in zero magnetic field plotted as a function of $1/\sqrt{T}$. $\Delta R \equiv R(T) - R_{800}$ where R_{800} is the sample resistance at 800 mK. The straight lines are guides to the eye. The vertical axis on the figure is 1% full scale.

of sample 2, which was grown in the same batch as the other whiskers, continues to decrease with temperature. If, on the other hand, this reduction in L_φ came about because of enhanced inelastic surface scattering (possibly caused by paramagnetic impurities in the GE varnish which coats the whiskers) then, since sample 2 is much thicker than the other samples, we would expect it to be less affected, and so display the observed persistent metallic behaviour.

4. Longitudinal magnetoresistance

In an effort to search for field-induced superconductivity, we performed longitudinal magnetoresistance measurements on samples 8 and 9. As we increased the magnetic field (at fixed temperature) both samples had the expected [13, 14] small maximum in $R(H)$ at about 0.3 T where the cyclotron radius matches the radius of the whisker. While the resistance of sample 8 was otherwise only weakly dependent on H, the resistance of sample 9 increased monotonically with the field by an amount that indicated the whisker was actually about 6° out of alignment with the field. The temperature dependence of the resistance of sample 9, at a fixed field of 9 T, is shown in figure 2. As can be seen from the figure, we find no evidence for superconductivity in this sample. Sample 8 (measured only in a field up to 6 T) also did not exhibit any features that could be associated with the onset of superconductivity.

While our data do not show any signs of high-field-induced superconductivity, we cannot conclusively rule out the predicted effects. It is possible that these samples are too disordered (this is certainly the case for sample 8). It may also be the case that, since cooling electronic systems to the low millikelvin temperature range is extremely difficult, the true electron temperature of the sample did not even reach 20 mK. Finally, it is also not known whether the strong spin–orbit scattering in bismuth would destroy the multivalley superconductivity.

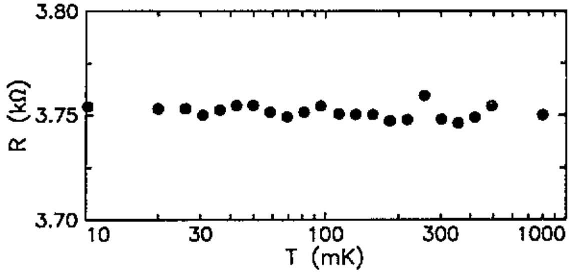

Figure 2. Temperature dependence of the resistance of sample 9 in a longitudinal ($I \parallel H$) magnetic field of 9 T.

5. Transverse magnetoresistance

Figure 3 shows the transverse magnetoresistance of sample 2 at 100 mK at fields up to 9 T. At low fields, $R \propto H^2$, while at higher fields, R increases more slowly, but does not saturate. This is qualitatively the same behaviour as is observed in the classical magnetoresistance of bulk Bi crystals [15]. The sample exhibits very weak Schubnikov–de Haas (SDH) oscillations, similar to those seen in small Bi wires [14]. The other three samples exhibited a similarly large transverse magnetoresistance, but the expected SDH oscillations were unobservably small, presumably due to the greater disorder in these whiskers.

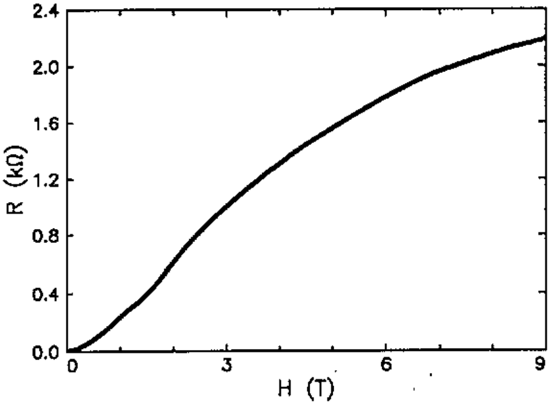

Figure 3. Resistance of sample 2 at a temperature of 100 mK as a function of transverse ($I \perp H$) magnetic field. The zero-field resistance of the sample is 4.3 Ω.

In previous studies of polycrystalline Bi films and wires [12, 16, 17], the small electron mobility μ ensured that the classical magnetoresistance ($\propto \mu^2 H^2$) remained a small perturbation on the magnetoresistance due to weak localization. Because the large classical magnetoresistance exhibited by our whiskers far exceeds the expected magnitude of such quantum mechanical corrections to the conductivity, we have attempted to investigate these corrections by measuring the temperature dependence of the sample resistance in fixed magnetic field. Figure 4 shows the results of such a measurement on samples 2 and 8. Between 100 and 800 mK, the sample resistance at high fields exhibits a clear logarithmic dependence on the temperature. It is also apparent that for $H > 0.5$ T, $\Delta R/R$ scales roughly with the sample resistance: evidence that the observed change is connected with quantum mechanical corrections to the conductivity. From the data, we find that $\Delta\sigma \sim 0.5$ $(\Omega\ \mathrm{cm})^{-1}$, and is approximately independent of the magnetic field. At the lowest temperatures, the temperature dependence of the resistance flattens out, presumably as a result of Joule heating.

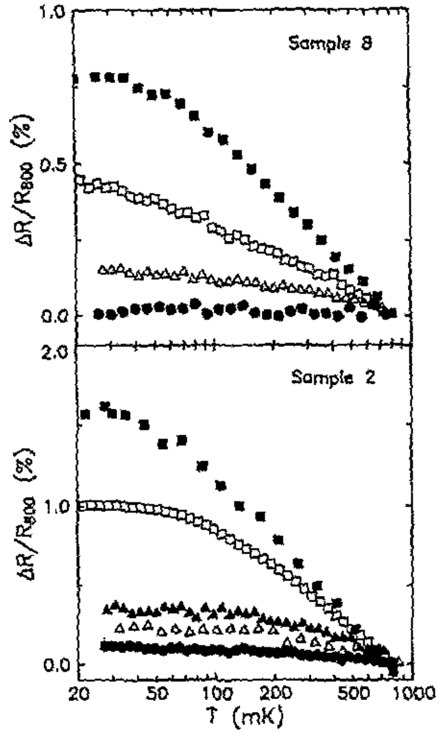

Figure 4. Percentage change in the transverse magnetoresistance of samples 2 and 8 as a function of temperature at several magnetic fields: ●, 0.5 T; △, 1.0 T; ▲, 2.0 T; □, 4.5 T; ■, 9.0 T. The vertical axis is as defined in figure 1.

Because of the relatively large applied magnetic fields, we can rule out ordinary weak-localization effects as an explanation for this behaviour. The magnitude of electron–electron interaction corrections, on the other hand, should remain unaffected by the field, since the effect of the Zeeman splitting should be largely washed out by the strong spin–orbit scattering in Bi [2]. If we assume that the samples are still effectively one dimensional, in spite of the vary small magnetic length (86 Å at 9 T) in these high fields, then we find that interaction effects can account—within a factor of 2 or 3—for the observed resistance changes.

The logarithmic temperature dependence of our data, which is usually indicative of two-dimensional behaviour, is somewhat problematic. The dimensionality of interaction effects depends on the thermal length L_T [2]. As mentioned above, the magnitude of the resistance rise indicates that L_T is not substantially changed from its zero-field value. In that case, transport in the whiskers should be one dimensional, and we would expect $\Delta R/R$ to vary as $T^{-1/2}$, in clear disagreement with our data. If L_T were substantially reduced by the applied field, then transport in the samples should be three dimensional, in which case interaction effects would predict $\Delta R/R \sim T^{1/2}$. While this temperature dependence is closer to what we observe, it is still not in very good agreement with our data. Neither do the data fit a cross-over from $T^{1/2}$ at high temperatures to $T^{-1/2}$ at lower temperatures. It therefore seems quite plausible that the samples are effectively two dimensional in high fields. While this may appear to be surprising behaviour for a wire-shaped sample, it is known that systems with a large classical magnetoresistance can exhibit a static skin effect [8] in which most of the electrical conduction is confined to a thin layer at the surface of the sample. If we assume that the dominant conduction path is indeed a thin sheath at the surface of the sample, we find that the interaction effect in two dimensions predicts a change in the sample resistance of the order of 1% between 800 and 100 mK for both samples. It is difficult to make a rigorous comparison, because it is not known over how much of the sample circumference this sheet extends.

Other possible mechanisms which could explain the observed low-temperature decrease in conductivity are magnetic freeze-out and magnetic-field-induced localization; however, neither the field or temperature dependence of our data match the $R \propto \exp(bH^2/T^{1/4})$ form predicted for these effects [6].

6. Conclusion

In summary, we have used electrical transport in bismuth whiskers both to search for collective behaviour and to study electron–electron interaction effects in relatively clean systems. We find that below 1 K, the zero-field resistance of our samples increases with decreasing temperature, in contrast to what was found in previous studies [9]. In strong perpendicular magnetic fields $H > 0.5$ T we observe a nearly field-independent conductance correction which we attribute to electron–electron interaction effects. On the basis of its logarithmic temperature dependence, it is possible that the dominant contribution to this correction comes from changes in the conductivity of a two-dimensional surface layer. We have also searched for a predicted triplet-paired multivalley superconducting state in a parallel field of 9 T down to 10 mK, but detected no signs of the onset of such a novel phase in bismuth.

Acknowledgments

We are grateful to E P Stillwell and M J Skove for advice on growing the whiskers, and to the Cornell Microkelvin Laboratory, where some of this work was performed. We wish to thank Y K Kwong, J M Parpia, R Thorne and P Santhanam for useful discussions. This work was supported by the NSF under Grant No DMR-9011562 and through the Cornell Materials Science Center via Grant No DMR-8818558-A02, and by the Academy of Finland. Fellowship support to GN was provided by the IBM Research Division.

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