Magnetic Resonance Evidence for Superconductivity in a Semimetal

I.P. Goudemond, G. J. Hill and M.J.R. Hoch

Department of Physics and
Condensed Matter Physics Research Unit,
University of the Witwatersrand, Johannesburg

1. Introduction

The group V semimetals As, Sb and Bi have low carrier densities and may be viewed as rather poor metals. Their electronic properties have been studied using a variety of methods, including NQR [1], [2]. At temperatures below the Debye temperature the nuclear spin–lattice relaxation rate in As and Sb has been found to obey the Korringa relation [1], [2]. For As, this relation has been found to hold down to 150 mK [3].

In the present work T_1 measurements on As have been extended to still lower temperatures. Motivation has come from the interesting electrical conductivity behaviour found by Uher [4] for a single crystal sample in the vicinity of 100 mK. These results may be interpreted as evidence for a superconducting transition, although no further experiments appear to have been carried out to confirm this. Probing of the superconducting state in zero magnetic field using NQR methods offers interesting challenges and opportunities.

2. Experimental Details

The experiments were carried out in an Oxford dilution refrigerator using procedures that have been described previously [3]. Pulsed NQR spin echo methods with signal averaging were used at 23.5 MHz on a powdered As sample. (^{75}As has $I = {}^3/_2$ and 100% abundance). The powdered material was prepared by crushing and sieving (25 μ mesh) high purity (99.9995%) arsenic, followed by annealing in vacuo and further careful sieving. An oxide layer on the surface of the grains prevented metallic contact between neighbouring particles.

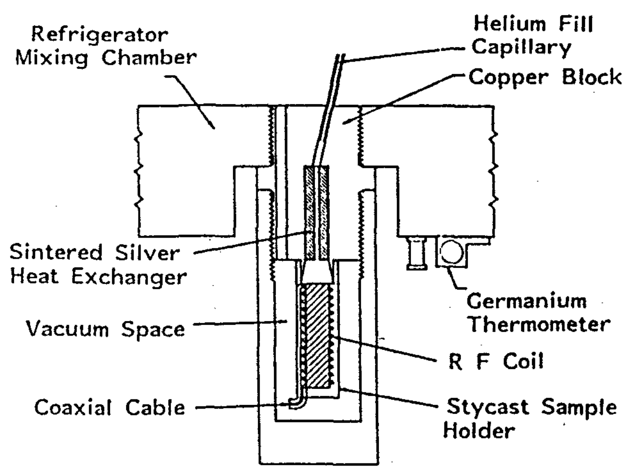

Figure 1
Sample holder and rf coil assembly for NQR measurements in the dilution refrigerator. The sample is immersed in liquid ^{4}He, which is in contact with the sintered silver heat exchanger.

Figure 1 depicts the sample arrangement used to ensure good thermal contact to the refrigerator mixing chamber. Liquid ^{4}He surrounds the sample and is in contact with a sintered silver heat exchanger. Further details may be found in reference [3]. Fractional rf pulses were used to minimize heating effects. Temperatures were measured using a calibrated germanium thermometer mounted on the mixing chamber.

3. Results and Discussion

In an effort to establish that the sample was in good thermal contact with it's surroundings, careful measurements of the echo amplitude were made as a function of temperature down to the lowest temperatures reached in these experiments, 40 mK. Down to 150 mK Curie law type behaviour is observed. At lower temperatures the data depart from linear behaviour. We do not believe that this is due to heating effects or the loss of thermal contact. Changes in the pulse sequence repetition rate did not change the amplitude of the echo signal. It is likely that some mechanism, characteristic of the sample, is responsible for the departure from Curie law behaviour.

At temperatures of 4 K and below, the skin depth δ at 23.5 MHz is comparable to, or less than, the mean particle radius r. We estimate that $\delta \sim 3.0$ μm at 150 mK, while $r \lesssim 10$ μm. It is clearly desirable that smaller particles should be used, although this is difficult because of rapid surface oxidation which occurs in air and the tendency of the arsenic particles to sinter during annealing.

Taking into account the attenuation of rf pulses and the presence of a core of undisturbed spins in the particles, we have examined the situation in some detail. In order to see whether spin diffusion can operate between spins near the surface of a particle and those in the interior, we have calculated the spin diffusion coefficient $D = {}^1/_{30}\ \sqrt{M_2 d^2}$, where M_2 is the second moment and d the spin spacing, and obtain $D \sim 2 \times 10^{-13}$ cm^2s^{-1}. On the time–scale of our experiments ($10^2 - 10^3$ s) spin diffusion operates over a distance $\sqrt{2Dt} \sim 10^{-1}$ μm. It may be concluded that this mechanism should have negligible effects on our results.

The change in the skin depth with temperatures below 1 K is of the order of 1 to 2%, which our calculations show will not lead to detectable changes in the echo amplitude beyond the Curie law changes. We do not believe that the departure from Curie law behaviour is due to effects of this kind.

The measured spin lattice relaxation rates are shown as a function of temperature in Figure 2. Note that, for magnetic relaxation in an $I = {}^3/_2$ system, a unique relaxation rate may be defined using $1/T_1 = 6\ W_{m}$, where W_{m} is the transition rate between the $\pm{}^1/_2$ and $\pm{}^3/_2$ spin states.

At temperatures down to roughly 120 mK the data obey the Korringa relation. Below this temperature the relaxation rate decreases less rapidly with T than expected from the Korringa relation. Figure 2 also shows the electrical conductivity data of Uher [4] in the same temperature range as the present measurements. It can be seen that the conductivity starts to decrease quite rapidly at ~100 mK. Inspection of the two plots in Figure 2 suggests a common underlying physical mechanism for the changes in behaviour observed in this temperature range.

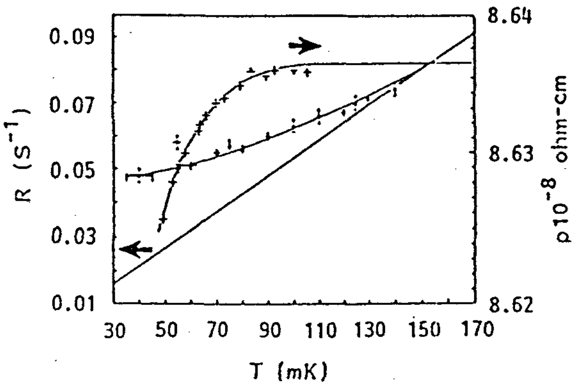

Figure 2
Plots of the ^{75}As spin lattice relaxation rate and of the resistivity of a single crystal arsenic sample [4] as a function of temperature down to 50 mK. The straight line which joins with the relaxation rate plot represents an extra— polation of the Korringa relation for arsenic found at higher temperatures.

It appears likely that a fairly broad superconducting transition occurs with a T_c around 100 μK. The T_1 data suggest a slightly higher T_c value than the conductivity data.

Cohen [5] has pointed out that the semimetals may be candidates for superconductivity through a BCS pairing mechanism. This is largely because of the multivalley character of these materials. On the basis of calculations given by Cohen for systems of this kind, a T_c of 100 mK is not unreasonable for As. Doped Bi has been found by Uher and Opsal [6] to have a $T_c < 100$ mK, depending on the concentration of the Sn or Te dopant.

We have attempted to fit the observed relaxation data for As using the Hebel–Slichter expression based on BCS theory. Anisotropy of the gap is allowed for by introducing a parameter $r = \Delta_0(0)/\Delta$, where Δ_0 is the BCS gap at 0 K and Δ is a measure of the gap anisotropy. However the theoretical curve does not fit the experimental data plotted in reduced form. Details will be given elsewhere. It is quite possible that the suggested transition in As is not of the standard BCS type. It appears, however, that other effects could be important.

Cohen [5] suggests that the semimetals will become type II superconductors with rather low upper critical fields. In the NQR experiment rf fields of 30 or 40 G are used and it is possible that some remnant field effects may be produced in the sample which contribute to relaxation.

Further experiments should be carried out to confirm the onset of superconductivity in As around 100 mK. Clearly, Meissner effect measurements should be attempted. Further NQR experiments involving CW methods with low rf fields may prove useful and complementary to the present measurements.

4. Conclusion

Evidence has been obtained of marked departures from Korringa relaxation behaviour in As below 120 mK. Taken together with previous electrical conductivity results, it appears likely that the anomalous behaviour is due to the onset of superconductivity.

The relaxation rate measurements are not in agreement with the Hebel–Slichter theory predictions. Further work is required to determine whether this is because of the non–BCS nature of the transition or some other cause, such as the magnitude of the rf fields used in our pulsed NQR experiments.

5. References

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