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Magnetoresistance below 1 K and temperature cycling of ruthenium oxide–bismuth ruthenate cryogenic thermometers

R.G. Goodrich*, Donavan Hall*, Eric Palm† and Tim Murphy†

*Department of Physics and Astronomy, Louisiana State University, Baton Rouge, LA 70803-4001, USA
†National High Magnetic Field Laboratory, Florida State University, Tallahassee, FL 32306-3016, USA

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The magnetic field dependence of the resistance of commercial 1000 Ω thick film chip resistors between 0.03 and 0.6 K in fields from zero to 18 T for five resistors and up to 32 T for one of those five shows both a positive and a negative magnetoresistance that is temperature dependent. In the field range between 4 and 32 T, and over the temperature measurement range, the resistance is proportional to $B^{1/2}$, and once an individual thermometer is calibrated, it can easily be used to determine the temperature at any field within the range. Measurements of the effect of repeated thermal cycling of these resistors from 300 to 77 and 4.2 K show that the resistance continually changes up to 120 cycles to 77 K or below then becomes stable. © 1998 Elsevier Science Ltd. All rights reserved

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Since the first publications reporting the properties of RuO_2 plus $Ru_2Bi_2O_7$ thick film chip resistors for use as cryogenic thermometers[1–3], these types of resistors have been employed for the measurement of low temperatures in many laboratories. Thermometers having a room temperature resistance of 1000 Ω are most useful below 1 K and have a large temperature coefficient of resistance in this range. A typical calibration curve for one such thermometer, labeled R2 below, is shown in *Figure 1* and its sensitivity function, d(ln *R*)/d(ln *T*), is shown in *Figure 2*. Thermometers made from chip resistors are useful because of their small size, low cost, and a magnetoresistance comparable to carbon glass. They are ideal for use in the temperature range 0.025 to 4 K[3–6]. In general, the 1 kΩ resistors can be used to measure temperatures up to about 40 K with reasonable sensitivity. Above 100 K, the resistance *versus* temperature curve is not monotonic. No systematic results for several resistors concerning the mag-

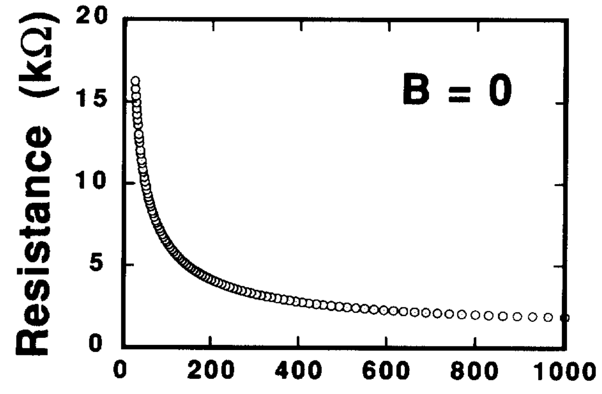

Figure 1 Resistance as a function of temperature from 25 to 100 mK for R2

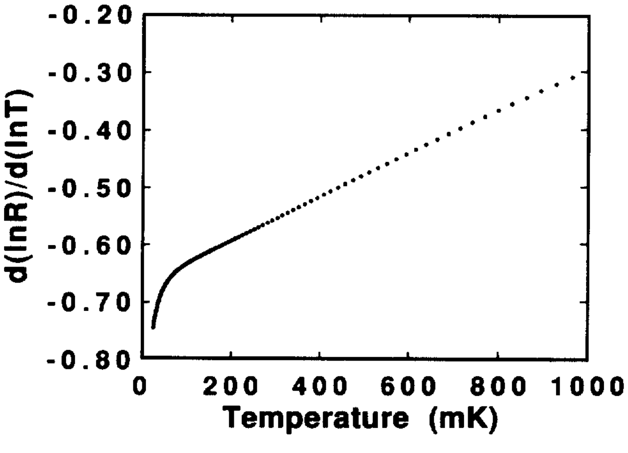

Figure 2 Temperature dependence of the sensitivity function d(ln *R*)/d(ln *T*) of R2

netoresistance below 1 K and stability upon temperature cycling have been published to date.

Measurements

Magnetoresistance

We have made measurements below 1 K of the magnetic field dependence of the resistance of five thick film chip resistors having a nominal resistance at room temperature of 1000 Ω. One calibrated thermometer mounted in a can was obtained from SI[7] (labelled R1). Four resistors (R2, R3, R4, R5) were purchased directly from Dale Electronics, Norfolk, Nebraska, USA (Model RCWP-575) and measured without packaging. The measurements on the packaged SI thermometer were performed at LSU with R1 emersed in the mash of a bottom loading non-metallic dilution refrigerator in fields between zero and 16 T. Measurements on the unpackaged R3–R5 were performed at the National High Magnetic Field Laboratory (NHMFL) emersed in the mash of a top loading dilution refrigerator in fields between zero and 18 T. One of the resistors, R2, was measured to 32 T in a ^{3}He refrigerator using an NHMFL resistive magnet. The resistors R3–R5 had been temperature cycled at least 60 times to 77 K, and the SI calibrated thermometer had been cycled to stability before the field dependent measurements (see below).

The four measured temperatures at which measurements on R1 were made were obtained from the zero field sensitivity curves provided by SI for this thermometer and agree with other thermometers (calibrated Ge above 0.075 K and nuclear orientation below 0.1 K) at zero applied magnetic field. Below 0.05 K this thermometer started to lose thermal contact with the bath and extremely long (> 0.5 h) times to reach equilibrium were required. The data on R1 were recorded between zero and 16 T during field sweeps at a rate of 0.05 T min^{-1} and include data for both increasing and decreasing field sweeps. During all of the measurements another thermometer mounted on the top of the mixing chamber and in a region where the field never exceeded 100 gauss was monitored and found not to change. The resistances measured from the field sweeps were checked at constant field intervals of 1.0 T for both increasing and decreasing fields and were found to give the same values obtained during the field sweeps. The R1 resistance measurements were made with a low power AC resistance bridge (RV-Elektroniikka, Model AVS-46).

At the NHMFL, R3–R5 were measured in a top loading dilution refrigerator at 0.028 K from zero to 18 T in a superconducting magnetic system and one of them, R2, was measured at 0.62 K from zero to 32 T in a resistive magnet. These resistors were mounted either emersed in the ^{3}He–^{4}He mixture of a dilution refrigerator, or in the ^{3}He liquid of a single shot ^{3}He refrigerator. For the dilution refrigerator measurements the magnetic field was swept both up and down at a rate of 0.33 T min^{-1}, and in the resistive magnet the sweep rate was 0.533 T min^{-1}. In both cases these sweep rates were sufficiently low for the magnetoresistance to reproduce between up and down sweeps and no changes occurred when the sweeps were stopped. In the NHMFL dilution refrigerator four wire measurements were done with an excitation current of 10^{-8} A at 13 Hz with the voltage across each resistor measured with a lock-in amplifier. It might be noted that another chip resistor was measured during the low temperature measurements of R3–R5, but the data shows evidence of bad electrical contact with the measured resistance values jumping up and down during all of the field sweeps. At the higher temperature used in the resistive magnet a Conductus Model LTC-20 resistance bridge was used with a 1 mV excitation and the ^{3}He vapour pressure monitored during the field sweeps.

Temperature cycling

In measurements on a separate set of five resistors, we have measured the stability of the resistance of chip resistor thermometers upon repeated cycling from room temperature to 77 and 4.2 K of four (labeled R6–R9) nominally 1000 Ω thick film chip resistors from the same batch purchased directly from Dale Electronics and one uncycled and uncalibrated packaged thermometer from SI (R10). For all of the cycling measurements the resistors were embedded in thermally conducting epoxy on a copper cylinder mounted on the end of a long stainless steel tube that could be immersed in either liquid nitrogen or liquid helium. The measurements at liquid nitrogen temperature were done in an open container filled to the same depth for each cycle with the copper cylinder immersed to the bottom of the cryostat. More care was taken in the nominally 4.2 K measurements. Prior to each cycle, the liquid helium depth in a storage dewar was measured so that the copper was six inches below the surface for each cycle. Resistance values were recorded only after the system came to equilibrium and the readings ceased to change. Atmospheric pressure was measured with a mercury manometer and recorded at the time of each cycle; and calculations of the temperature of the liquid helium were made. On each cycle the temperature at which the reported resistance values are listed as 4.2 was the same to within 0.001 K. All of these DC resistance measurements were made with a four wire connection to each resistor using a Hewlett Packard Model 3457A multimeter (10^{-4} A excitation current, corresponding to the 30 kΩ scale). The excitation level used is higher than that recommended for use in situations where the user wishes to avoid heating, but using high excitation currents yields more stable readings. It should be noted that we did not observe any evidence of heating in this measurement configuration; this was checked by changing to lower excitation currents and monitoring the resistance of the chip.

Results

Magnetoresistance

For the chip resistors at the lowest temperature of measurement, 0.028 K, the magnetoresistance becomes large and negative at low fields then reverses direction heading back to zero at higher fields, but not crossing the zero resistance change line below 18 T. The results for R3–R5 are shown in *Figure 3* for data from a 0.33 T min^{-1} down sweep. As is clearly seen, the magnitude of the negative magnetoresistance change increases with the magnitude of the zero field resistance.

For the measurements on R3–R5 at the NHMFL, near zero field for increasing field sweeps a large positive spike in the resistance is seen as the sweep is started before the magnetoresistance becomes negative. This effect is enhanced when the sweep rate is increased to 0.66 T min^{-1} and is decreased in the down sweeps. Thus, the magnitude

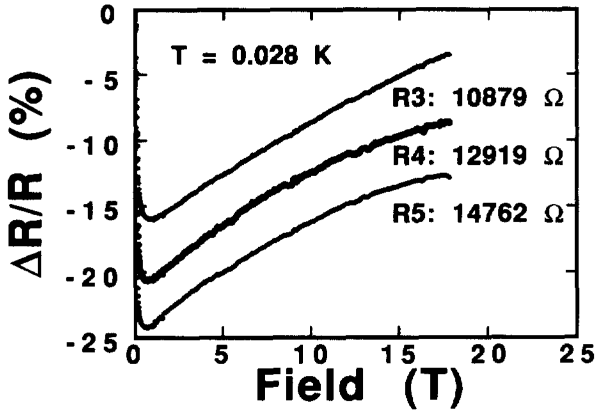

Figure 3 Percentage resistance change as a function of applied magnetic field for R3, R4, and R5 at 0.028 K between zero and 18 T. The zero field resistances for each resistor are listed on the graph

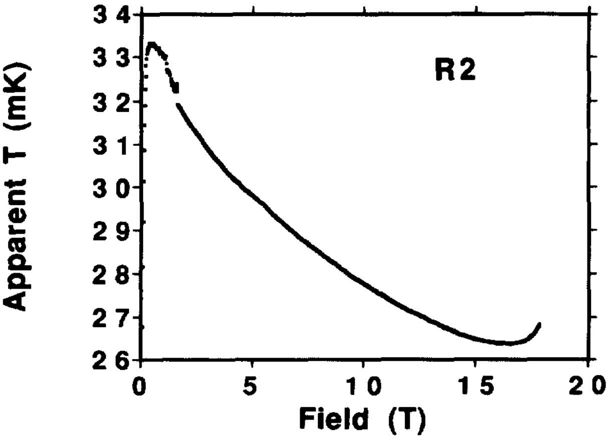

Figure 5 Apparent temperature of R2 obtained from the zero field calibration between zero and 18 T at 0.028 K

of this spike is sweep rate and sweep direction dependent. We do not know the origin of this spike or whether it is intrinsic to the resistors. An attempt was made to reduce the flux jumping near zero field in the Nb_3Sn magnet that could cause voltage spikes in the leads, but this did not remove the spikes.

The same negative magnetoresistive behaviour is seen in R1 at higher temperatures of 0.084 K (three times the temperature at which R3–R5 were measured) and 0.117 K, but the magnetoresistance becomes positive at less than 5 T at these higher temperatures. At temperatures of 0.142 K and above, the magnetoresistance is entirely positive with the total change becoming much smaller as the temperature is raised. No zero field positive resistance jumps were observed in the R1 data where very slow sweep rates were used. The R1 results are displayed in *Figure 4*.

Taking the most extreme example, we have calculated the apparent temperature change at 0.028 K by fitting the zero field calibration data and calculating ΔT as the difference between the zero field field temperature value and the temperature calculated using the curve fit from the resistance measured in fields between zero and 18 T for R4 as shown in *Figure 5*. This is the temperature range where the largest resistance change for a small change in temperature occurs and corresponds to a change of about 25% in temperature at the maximum negative magnetoresistance.

At 0.62 K the total resistance change of R2 is about 20% at 32 T. In the higher temperature measurements, which used the resistive magnet, no initial sharp resistance increase is observed even though a much higher sweep rate was used. For the 0.62 K measurements, the vapour pressure of the ^3He bath was monitored during the field sweep and found to change less than 0.01 mbar, corresponding to a temperature change of < 5 mK. However, the overall resistance change of 20% is an apparent temperature change of 0.175 K.

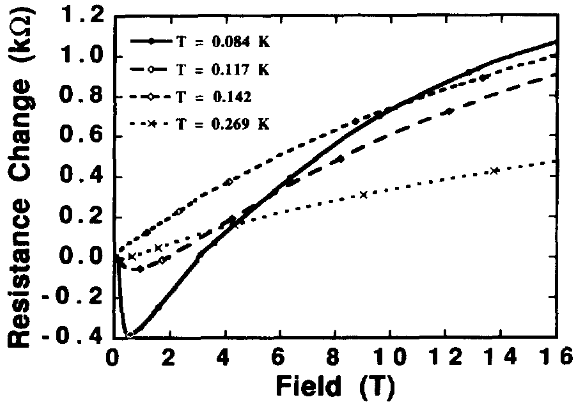

Figure 4 Resistance change for R1 (0.270, 0.14, 0.12, and 0.08 K) as a function of applied magnetic field

Temperature cycling

Measurements were made over a period of three months on five chip resistors with a total of 98 complete temperature cycles. For each cycle, the following procedure was performed on each of the five resistors: (1) an ambient room temperature measurement; (2) a 77 K measurement; (3) another room temperature measurement; (4) a 4.2 K measurement; and (5) a final room temperature measurement. Thus, each resistor was cycled from room temperature to 77 K or below 196 times. These chip resistors have been designed to be nearly temperature independent at room temperature. They are stable to within ± 100–200 ppm K^{-1} for ± 50 K around 300 K, and therefore show no significant change in resistance with small variations in room temperature. Because of this, it was not necessary to employ a controlled room temperature bath.

These 1000 Ω resistors are most useful for temperature measurements below 4.2 K, and we show in *Figure 6* the results for each resistor of the 4.2 K resistance measure-

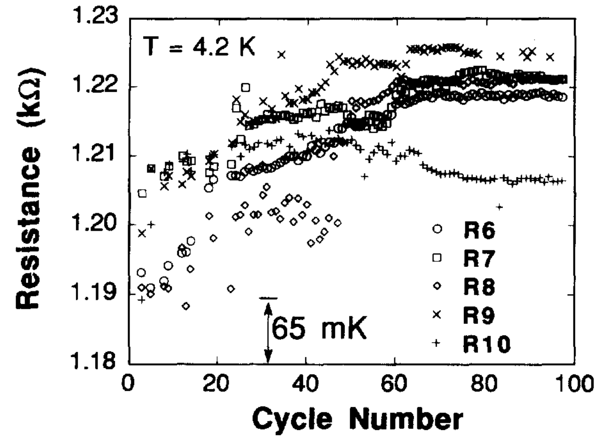

Figure 6 Resistance for five resistors at 4.2 K during temperature cycling

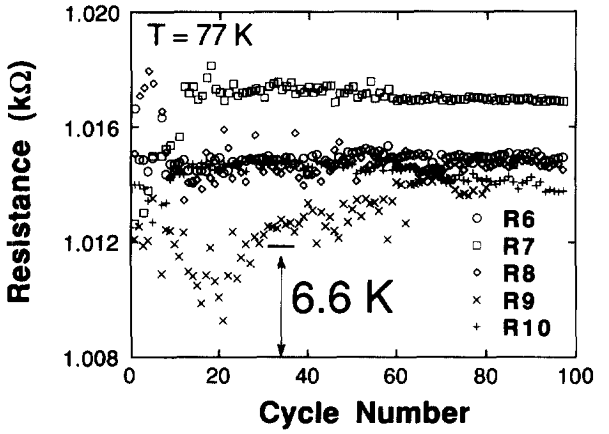

Figure 7 Resistance for five resistors at 77 K during temperature cycling

ments as a function of cycle number. All of the resistors showed an initial increase in resistance with temperature cycling. The change in resistance in the first 60 cycles (120 to 77 K and below) is significant. From calibrations on other resistors of this type the average observed 30 Ω change corresponds to approximately 0.2 K at 4.2 K. After 40 to 50 cycles they began to become more stable, but two (R7 and R8) showed a definite jump after 50 cycles and one (R7) lost contact during some cycles after 77 cycles. The temperature cycling of the epoxy causes it to crack and probably led to the intermittent open circuit in R7 at low temperatures. In each case, the resistance changes upon cycling between 300 and 4.2 K became stable to within approximately ± 1 Ω (± 0.03 K) out of 1200 Ω for each successive cycle. The initial increase in resistance with cycling is evident in both the initially uncycled commercial resistor that is mounted in a gas filled can and in the resistors embedded directly in epoxy. Therefore, it would appear that the temperature cycling effect is due to the resistance element, substrate, and glass enclosure, rather than to the mounting or lead connection method.

The 77 K and 300 K results are shown in *Figures 7* and *8*. The resistance changes at 77 K are more erratic, but also tend to stabilize after approximately 60 cycles (note that 120 cycles to 77 K or below are made for the 60 77 K readings). Part of the scatter in the 77 K data is due to the fact that no attempt was made to control the temperature of the liquid nitrogen in the open container. Depending on the amount of absorbed oxygen in the nitrogen bath, the temperature could have changed by several degrees. Both the nominal 77 and 300 K results mirror the 4.2 K changes in that both become more stable after 60 cycles. The 300 K results are actually a better indicator than the 77 K results to predict stability of the 4.2 K resistances. This is partially due to the fact, mentioned above, that these resistors have been specifically designed to have a low temperature coefficient of resistance around 300 K and variations in room temperature have little effect. This result also indicates that the cycling resistance changes are intrinsic to the chip resistors resistive element.

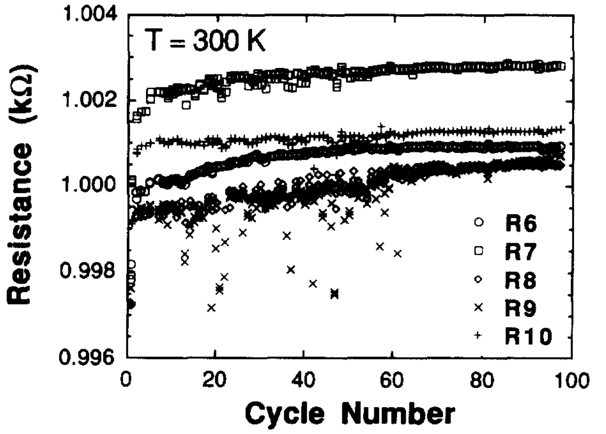

Figure 8 Resistance for five resistors at 300 K during temperature cycling

Discussion

Below 0.150 K the magnetoresistance of chip resistors is negative at low fields, crosses the zero field value, and becomes positive at higher fields. This type of behaviour generally agrees with that found in reference 3, and is presumably due to weak localization[8]. Above 0.2 K the magnetoresistance is entirely positive and overall decreases as the temperature is increased. At all measured temperatures the resistance measured above 4 T is a monotonically increasing function of applied field, and is directly proportional to $B^{1/2}$ for all temperatures and resistors. In *Figure 9* we show the magnetoresistance of R1 and R2 plotted against $B^{1/2}$ for five of the measurement temperatures. It can be seen that this behaviour covers a wide temperature and field range. Resistor R2 exhibits the $B^{1/2}$ field dependence at 0.62 K from about 3 to 32 T as shown in *Figure 10*. This square root dependence on the field is what might be expected from the conduction mechanism experiencing weak localization with correlations[9], i.e. electron–electron scattering. While the field dependent resistance curves vary from resistor to resistor depending on the individual zero field resistances, and perhaps the production batch, at the same temperature, the same general field dependent properties are observed in all resistors. From this data on a limited number of samples it can be seen that thermometers of this type can be calibrated for use in high magnetic fields, but for accurate measurements of temperature should be done so on an individual basis.

The major conclusion to be drawn from the temperature cycling results is that, if chip resistors are to be used as

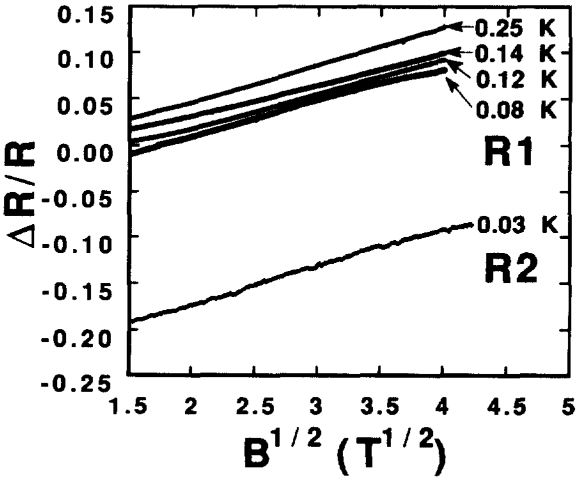

Figure 9 Square root dependence of resistance change on applied magnetic field between 2.5 T and the maximum measurement field for two resistors, R1 and R2, at five temperatures

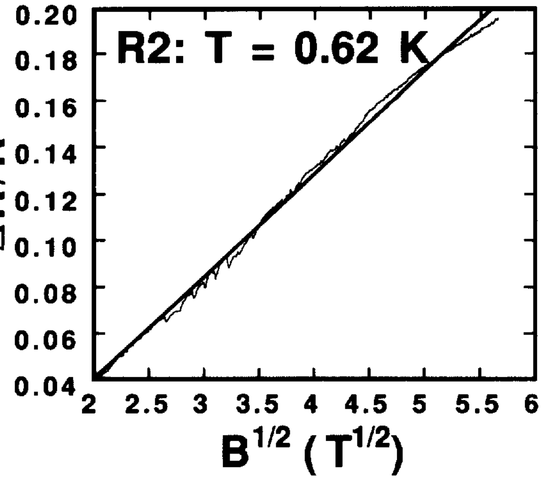

Figure 10 Square root dependence on applied magnetic field of resistance change between 3 and 32 T for R2 at 0.62 K

calibrated thermometers, the calibration should not be done until at least 120 cycles to below 77 K have been done. However, one only needs to record room temperature resistance values to determine when the resistance values have become stable. Given that it is probable that microcracking is responsible for the resistance changes observed during repeated cycling, it is reasonable to take precautions to prevent excessive heating above room temperature of a calibrated chip resistor to ensure that annealing of the microcracking does not undo the calibration.

Acknowledgements

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References

1. Koppetski, N., *Cryogenics*, 1983, **23**, 559.
2. Doi, H., Narahara, Y.U., Oda, Y. and Nagano, H. In *Proc. LT-17*, Karlsruhe, Germany, eds U. Eckern *et al.* North-Holland, Amsterdam, 1984, p. 405.
3. Li, Q., Watson, C.H., Goodrich, R.G., Haase, D.G. and Lukefahr, H., *Cryogenics*, 1986, **26**, 467.
4. Bosch, W.A., Mathu, F., Meijer, H.C. and Willekers, R.W., *Cryogenics*, 1986, **26**, 3.
5. Meisel, M.W., Stewart, G.R. and Adams, E.D., *Cryogenics*, 1989, **29**, 1168.
6. Uhfig, K., *Cryogenics*, 1995, **35**, 525.
7. Scientific Instruments, Inc., 4400 W. Tiffany Drive, West Palm Beach, FL 33407, USA.
8. Anderson, P.W., *Phys. Rev.*, 1958, **109**, 1492.
9. Alshuler, B.L., Khmelnitskii, D.E., Larkin, A.I. and Lee, P.A., *Phys. Rev. B*, 1980, **22**, 1542.