

# Doped $\text{GdCl}_3$ high resolution thermometers for use near to the lambda point

R.A.M. Lee<sup>a</sup>, A.W. Harter<sup>b</sup> and T.C.P. Chui<sup>a</sup>

<sup>a</sup>Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91109

<sup>b</sup>Condensed Matter Physics, California Institute of Technology, Pasadena, California 91125

The paramagnetic salt  $\text{GdCl}_3$  was doped with the diamagnetic  $\text{La}^{3+}$  ion, depressing its Curie temperature ( $T_c$ ) from 2.2 K to 2.185 K. A paramagnetic salt thermometer was constructed using this salt and measurements were made of its sensitivity, noise and drift.

## 1 INTRODUCTION

High-resolution thermometers (HRTs) were developed to study the superfluid phase transition of liquid  $^4\text{He}$ , which is the sharpest transition presently known. Temperature resolutions down to  $10^{-11}$  K/ $\sqrt{\text{Hz}}$  have been reported [1], allowing predictions of phase transition theory to be tested in microgravity, where the transition can be approached much closer than on Earth due to the elimination of the hydrostatic pressure gradient [2].

The HRT consists of a paramagnetic salt pill tightly coupled to a superconducting pick-up coil. A superconducting flux tube, surrounding the HRT, is used to trap a very stable DC field ( $\sim 10$  mT). The salt is thermally coupled to the helium sample through a grid of high purity (99.999%) copper heat fins. The pick-up coil is connected to a SQUID, which measures changes in the magnetization of the salt as a function of temperature. Ideally, these thermometers should be operated with the salt pill in the paramagnetic phase and close to  $T_c$  where its magnetization is highly temperature dependent. In the ferromagnetic phase, discontinuous changes in the flux density - the Barkhausen effect [3] - can appear as a significant noise contribution in the thermometer measurements. Most HRTs [4] use salt pills made of crystalline copper ammonium bromide  $[\text{Cu}(\text{NH}_4)_2\text{Br}_4 \cdot 2\text{H}_2\text{O}]$  (CAB) which has a  $T_c$  of approximately 1.8 K. Recent designs use  $\text{GdCl}_3$ , which is chemically less reactive than CAB and can be grown directly onto the copper fins. In addition,  $\text{GdCl}_3$  has a  $T_c$  of 2.2 K and is approximately five times as sensitive as CAB at the superfluid transition temperature,  $T_\lambda$  (2.1768 K under saturated vapour pressure).

Despite these favourable properties,  $T_c$  for  $\text{GdCl}_3$  lies just above  $T_\lambda$ , causing the salt to operate in the ferromagnetic phase. In an attempt to overcome this problem, a sample of  $\text{GdCl}_3$  was doped with  $\text{La}^{3+}$ , a non-magnetic ion, in order to depress its Curie temperature.  $\text{GdCl}_3$  and  $\text{LaCl}_3$  are isomorphous salts. In a solid solution, the diamagnetic  $\text{La}^{3+}$  ions substitute for the paramagnetic  $\text{Gd}^{3+}$  ions to form crystals in which both ions are present [5]. For a non-magnetic ion such as  $\text{La}^{3+}$ , the depression in  $T_c$  is expected to be approximately linear with doping concentration [6].

## 2 EXPERIMENT

### 2.1 Sensitivity measurement

The salt was prepared from 94.5 g of  $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$  and 2.7 g of  $\text{LaCl}_3$ , producing 63.74 g of  $\text{Gd}_{0.9585}\text{La}_{0.0415}\text{Cl}_3$ . The hydrated  $\text{GdCl}_3$  was first mixed with  $\text{LaCl}_3$  and then dehydrated, using a reflux condensing technique with thionyl chloride [7]. The mixture was heated in a dry nitrogen atmosphere until the sample melted. The molten salt was poured into a BeCu capsule, flowing in-between the enclosed copper heat fins, and left to solidify. The assembly was sanded to remove excess salt and sealed, using a BeCu cap and cadmium solder. BeCu was chosen in order to reduce background noise caused by current fluctuations in the capsule wall, while maximising thermal conduction to the salt pill. A superconducting pick-up coil fit tightly around the capsule. Its dimensions were optimised to match the input impedance of the SQUID and to cover the salt sufficiently to ensure maximum energy transfer. A Niobium capillary shielded the twisted pair leads of the pick-up coil. The capsule was soldered to an annealed, high purity (99.999%), copper rod that was in thermal contact with a helium reservoir (Fig. 1). A number of HRTs were constructed, three of which were mounted in thermal contact with the helium.

The helium reservoir was separated from a surrounding liquid helium bath by a three-stage thermal isolation system located inside a vacuum can. The first two stages were controlled to within  $10 \mu\text{K}$  using calibrated germanium resistance thermometers (GRTs). The third, and innermost, isolation stage formed a shield completely surrounding the reservoir and the HRTs. Its temperature was regulated to within  $0.1 \mu\text{K}$  by a servo system using a fourth HRT, which was made with a salt pill of pure  $\text{GdCl}_3$ . Sensitivity versus temperature measurements were made for both the pure and doped  $\text{GdCl}_3$  HRTs by slowly cooling the helium sample and recording the output of the HRTs and the GRTs simultaneously. The sensitivity of each thermometer is plotted versus temperature in Fig. 2. The sensitivity is defined as the change in the number of magnetic flux quanta,  $\Phi_0$ , recorded by the SQUID magnetometer over a given change in temperature, as measured by the corresponding GRT.

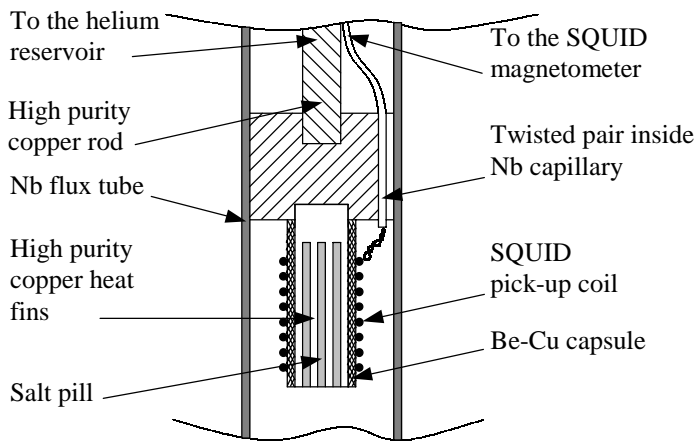


Figure 1 Schematic of the HRT

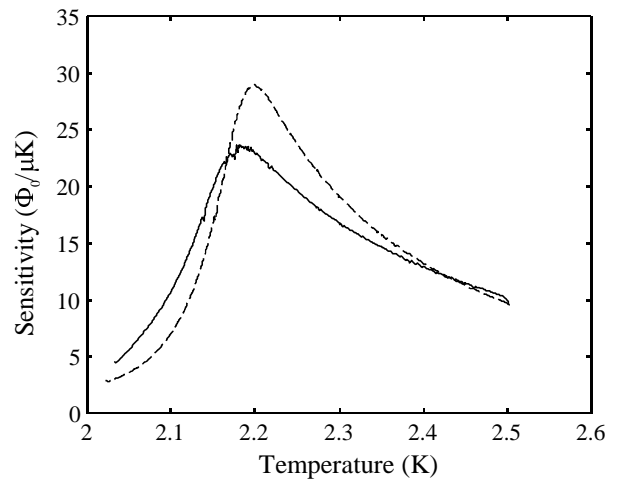


Figure 2 Sensitivity versus temperature data for  $\text{GdCl}_3$  (dashed line) and La doped  $\text{GdCl}_3$  (solid line) HRTs.

The pure  $\text{GdCl}_3$  HRT had a maximum sensitivity of  $28.9 \Phi_0/\mu\text{K}$  at 2.200 K, while the doped HRT had a maximum sensitivity of  $23.6 \Phi_0/\mu\text{K}$  at 2.185 K. This clearly demonstrates that the Curie temperature has been depressed. However, the depression in  $T_c$  by 0.7% was smaller than expected for a 4% La concentration [6], and this lower  $T_c$  is still above the temperature range for experiments conducted very near to  $T_\lambda$ . This may be due to inhomogeneous doping of the  $\text{GdCl}_3$  salt due to clustering of the  $\text{LaCl}_3$  while the salt solidified.  $\text{LaCl}_3$  has a melting temperature of  $860^\circ\text{C}$  compared to  $609^\circ\text{C}$  for  $\text{GdCl}_3$  [8]. The reduction in sensitivity, by 18%, is thought to be due to the anisotropic susceptibility of the  $\text{GdCl}_3$  crystals that were formed during solidification [9].

## 2.2 Noise measurement

To measure the HRT thermal noise density, the isolation system was adjusted such that the cooling rate was less than  $0.01 \text{ nK/s}$ . Measurements were taken  $5 \text{ mK}$  below  $T_\lambda$ . The output of the HRT was filtered at  $10\text{Hz}$ , connected to a spectrum analyser, and the power spectral density (PSD) determined. (Fig. 3)

In a thermometer, one source of fluctuation noise is temperature variation due to energy fluctuations through the thermal link to the reservoir. If all other sources of noise are negligible, this temperature noise defines a thermodynamic limit. The Fluctuation-dissipation theorem (FDT) predicts a specific relation for this thermal noise density [10,11]:

$$(T^2)_{f^+} = 4\tau k_B T^2 / C (1 + 4\pi^2 \tau^2 f^2) \quad (1)$$

where  $(T^2)_{f^+}$  is the power spectral density of temperature fluctuations, defined for positive frequencies. Here  $\tau$  and  $C$  represent the thermal relaxation time and heat capacity, respectively, of the salt pill. They are related by  $\tau = RC$ , where  $R$  is the thermal impedance between the salt pill and the helium sample. As can be seen, in the low frequency limit, Eq. (1) reduces to  $\sqrt{(4Rk_B T^2)}$ . Hence  $R$  is the only relevant parameter that can be adjusted in order to reduce noise originating from thermal fluctuations [1].

Agreement with the FDT can be determined by fitting Eq. (1) to the noise spectrum. This requires knowing the value of  $\tau$  and  $C$  for the salt pill. The heat capacity was measured directly by a heat pulse technique, with the helium reservoir empty. After taking into account the additional heat capacity of the copper reservoir, each salt pill was determined to have  $C = 82 \pm 2 \text{ mJ/K}$ . This agreed with an estimate of  $C$  calculated using the volume of the salt ( $0.24 \text{ cm}^3$ ), the density of  $\text{GdCl}_3$  ( $4.52 \text{ g/cm}^3$ ) [8], and the zero field heat capacity data of Hovi *et al* [12]. The thermal relaxation time was determined by observing the response of the HRT to a pulse of heat applied to the helium reservoir, when full. This yielded  $\tau \approx 1.0 \text{ s}$  which is consistent with the value determined from the fit to the noise spectrum,  $\tau = 0.7 \pm 0.1 \text{ s}$ . (Fig. 3) This gives an estimate for the thermal impedance of  $R = 8.5 \pm 1.5 \text{ K/W}$ . At low frequencies, the noise density was  $5 \times 10^{-11} \text{ K}/\sqrt{\text{Hz}}$ , which is equal to the noise density of HRTs made with salt pills of pure  $\text{GdCl}_3$  [1]. The PSD was found to contain a small but observable background noise due to Johnson current noise in the capsule assembly. This was confirmed from measurements of a ‘dummy’ capsule, where the salt pill was absent. By disassembling the capsule and taking noise measurements of each component, it was shown that most of the current noise originated from the copper heat fins, and not from the BeCu capsule or the copper thermal link. This background noise had a magnitude of approximately  $1.8 \times 10^{-4} \Phi_0/\sqrt{\text{Hz}}$ , corresponding to a PSD of  $5 \times 10^{-23} \text{ K}^2/\text{Hz}$ .

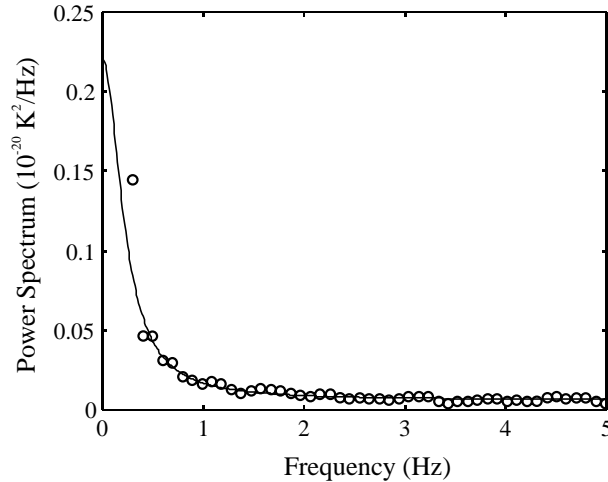


Figure 3 Noise spectrum for the La doped  $\text{GdCl}_3$  HRT (circles). FDT fit (solid line)

### 2.3 Drift measurement

All HRTs exhibit small drift rates that must be taken into account when making precise measurements over long periods. The origin of drift is thought to be due either to flux creep in the Niobium flux tube, or thermal relaxation of the salt pill that causes changes in its magnetization. It has been observed [13] that, following the initial cool down of the salt pill, the drift rate decays to a constant value over a period of several days. Even small temperature changes ‘re-energise’ the drift, which then decays with a faster time constant back to a steady value.

The drift rate was determined from measurements of the lambda point, taken over several hours, by slowly heating and then cooling through the superfluid transition. The lambda point was then used as an absolute temperature marker, to which any relative drift in the HRT flux output could be resolved. The drift rates of the doped HRTs were measured several times during a six-month run. They had constant drift rates of approximately  $5 \times 10^{-12}$  K/s, in a direction such that the lambda point appeared to drift upwards in temperature. Since all the HRTs drifted in the same direction there is also the possibility that the lambda point itself was drifting, due to a small reservoir leak through the fill line. The reservoir was filled at constant volume and sealed with a mechanical valve. This implies that the measured drift rate is an upper limit and may be smaller. For comparison, the drift rates of pure  $\text{GdCl}_3$  and CAB HRTs are  $\leq 10^{-12}$  K/s and  $\leq 10^{-13}$  K/s respectively [13].

## 3 CONCLUSION

The paramagnetic salt  $\text{GdCl}_3$  was doped with a 4% Lanthanum concentration, depressing its Curie temperature by 0.7%. With improved doping homogeneity it is proposed that this depression could be finely tuned as a function of the amount of Lanthanum added to the salt. The HRT low frequency noise levels ( $5 \times 10^{-11}$  K/ $\sqrt{\text{Hz}}$ ) and drift rates ( $5 \times 10^{-12}$  K/s) are equivalent to those of HRTs made with salt pills of pure  $\text{GdCl}_3$ . The noise spectrum is found to be in good agreement with the predictions of the Fluctuation-dissipation theorem, indicating that the thermodynamic noise limit has been reached. Further improvements in noise levels may be achieved by both carefully re-designing the HRT to reduce the current noise and reducing the thermal impedance between the salt pill and the helium sample.

## ACKNOWLEDGEMENTS

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