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Anomalous nuclear magnetic susceptibility of platinum powder

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The nuclear magnetic susceptibility of platinum powder has been measured in magnetic fields of 6.8, 13.7, and 27.4 mT as a function of temperature in the range 1–20 mK, as determined by the melting curve of ^{3}He. The susceptibility does not follow a Curie law, but the anomalous behavior at 13.7 and 27.4 mT fits a Curie-Weiss law with a field-dependent Weiss constant. The spin-lattice relaxation time does not conform to a Korringa relation. The results can explain the discrepancies in the pressure dependence of the transition temperature of superfluid ^{3}He measured by different groups.

There are a number of secondary thermometers in use at millikelvin temperatures, each of which is based on a different thermometric substance. Among the most commonly used are (i) the nuclear magnetic susceptibility of platinum, (ii) the magnetic susceptibility of lanthanum-diluted cerium magnesium nitrate (LCMN), and (iii) the melting curve of ^{3}He. The susceptibility of platinum has been assumed to obey Curie's law down to the lowest temperatures. If both Curie's law and the Korringa relation are obeyed then the nuclear susceptibility divided by the spin-lattice relaxation time T_1 is constant. The magnetic susceptibility of LCMN is assumed to follow a Curie-Weiss law with Weiss constant which is determined by comparison with another thermometer,[1,2] or inferred by other means.[3] In contrast, the melting curve of ^{3}He provides, in principle, a thermodynamic scale *proportional* to absolute temperature. The only thermodynamic determination of relative temperature, T/T_A, on the melting-curve scale is that made by Halperin, Rasmussen, Archie, and Richardson,[4] described below, and adopted here.

In this Rapid Communication we report on pulsed NMR measurements of the nuclear magnetic susceptibility of platinum powder[5] as a function of the temperature determined from the melting pressure of ^{3}He. The comparison was made in three magnetic fields of 6.8, 13.7, and 27.4 mT over a wide temperature range (1–20 mK). In 13.7 and 27.4 mT the temperature dependence of the susceptibility χ may be represented by a Curie-Weiss law $\chi = C/(T-\delta)$, where the Weiss constant δ is field dependent. The behavior in 6.8 mT is more anomalous. The previously reported discrepancies, in the determination of the superfluid transition temperatures of ^{3}He, between measurements based on the assumption of Curie law behavior for platinum powder and others based on the melting curve of ^{3}He may be accounted for by our results.

In our experiment both the platinum sample and the melting-curve thermometer were thermally coupled to the main heat exchanger of the ^{3}He cell, which was cooled by a conventional copper nuclear demagnetization stage. A sample of 0.95 g of platinum powder was contained in an epoxy tower and connected to the main heat exchanger via a 4-mm-diam column of liquid 30 mm in length. The melting-curve thermometer (MCT) was of similar design to that described by Greywall and Busch.[6] It contained 0.5 m^2 of silver sinter and was connected by silver wires (15 wires, 0.5 mm diam, 20 mm long) through an epoxy feedthrough to a separate silver sinter sponge (4-m^2 area) providing heat exchange to the liquid in the main heat exchanger. The residual external heat leak across this thermal link produced a negligible temperature difference (at most a few microkelvin) between the MCT and the liquid-^{3}He sample.[7]

The nuclear magnetic susceptibility of the platinum was measured by a commercial NMR spectrometer[8] and this was compared with the pressure in the MCT at different temperatures and under "equilibrium" conditions with the cell warming under the residual heat leak. Measurements were made at Larmor frequencies of 62.5, 125, and 250 kHz, corresponding to magnetic fields of 6.8, 13.7, and 27.4 mT. In each case the measuring field was trapped inside a niobium tube which surrounded the Stycast tower. The field on the MCT and the main heat exchanger was nominally zero.

The melting-curve temperature scale used from 1–25 mK was that established by Halperin *et al.*[4] in the form of melting pressure $(P-P_A)$ as a function of the relative temperature, $T^* = T/T_A$, where (P_A, T_A) are the coordinates of the superfluid A transition on the melting curve and T^* was determined thermodynamically. To do this, Halperin *et al.*[4] held a ^{3}He sample at constant pressure on the melting curve and measured the volume change ΔV resulting from the solidification of some solid on application of a heat pulse ΔQ. Then $T\,dP/dT = \Delta Q/\Delta V$ and integrating from (P_A, T_A) determined T^* in terms of $(P-P_A)$. Any systematic error ϵ estimated to be at most 2%, in the measurement of $\Delta V/\Delta Q$ gave rise to an error in T^* of $\epsilon|\ln T^*|$%. Above 25 mK we used the scale of Greywall.[9] Greywall determined T_A in terms of the superconducting transition temperature of tungsten [15.57 mK on the Nat. Bur. Stand. (U.S.) scale] and the thermodynamic scale of Ref. 4 to find $T_A = 2.708 \pm 0.11$ mK and this is the value adopted here. However, the results of our paper do not depend strongly on the exact choice of T_A, only that the melting-curve temperature scale should be *proportional* to absolute temperature.

The measured pressures of the standard low-temperature fixed points agree well with the earlier work; we find $P_B - P_A = 19.8 \pm 0.2$ mbar and $P_S - P_A = 52.3 \pm 0.2$ mbar.

We have also measured the superfluid transition temperature at several pressures, corresponding to a melting pressure $P_C(p)$, between 0.25 and 3.5 bars using the attenuation of ultrasound as an indicator of the transition. A linear extrapolation gives $P_C(p=0)-P_A=51.6\pm0.3$ mbar at zero pressure, which may be compared to the value 52.6 mbars found by Greywall.[9]

The platinum nuclear susceptibility results are shown in Fig. 1, in which $(\chi T)^{-1}$ is plotted against T^{-1} with the susceptibility data suitably normalized. If the susceptibility conforms to a Curie-Weiss law with Weiss constant δ the result should be a straight line of slope $-\delta$. The agreement with this form is excellent at 250 and 125 kHz giving δ values of 0.13 ± 0.03 and 0.265 ± 0.03 mK, respectively. The quoted error includes a contribution arising from the possible systematic errors in the thermodynamic T^* discussed earlier. At 62.5 kHz the behavior is more complex; a quadratic fit to T^{-1} gives $\delta=0.32\pm0.05$ mK as a high-temperature asymptotic value for the Weiss constant.[10]

Strong evidence that such anomalies in the nuclear susceptibility of platinum powder are a common feature of samples in use comes from the pressure dependence of the superfluid ^{3}He transition temperature $T_c(p)$. Comparison of $T_c(p)/T_A$ as determined by thermometry based on platinum, or by the melting curve, enables these secondary thermometers to be compared over a rather restricted temperature range 1–2.7 mK. This procedure is, however, subject to systematic errors due to the presence of small temperature gradients at low temperatures. It has been pointed out by Greywall,[9] and Parpia, Kirk, Kobiela, and Olejniczak,[2,11] among others, that it is possible to relate these scales by a temperature offset, whose physical significance is now apparent. The discrepancy between Greywall's determination of $T_c(p)$ using a melting-curve thermometer and results based on platinum thermometry at 250 kHz by Alvesalo, Haavasoja, and Manninen,[1] Feder,[12] and Hook[13] correspond to a δ of order 0.1 mK. If the determination of $T_c(p)$ by Parpia *et al.*[2] is used, somewhat higher values of δ result. In contrast the T_c values of Varoquaux,[14] also based on platinum thermometry at 250 kHz, give a value of δ for their sample of essentially zero.

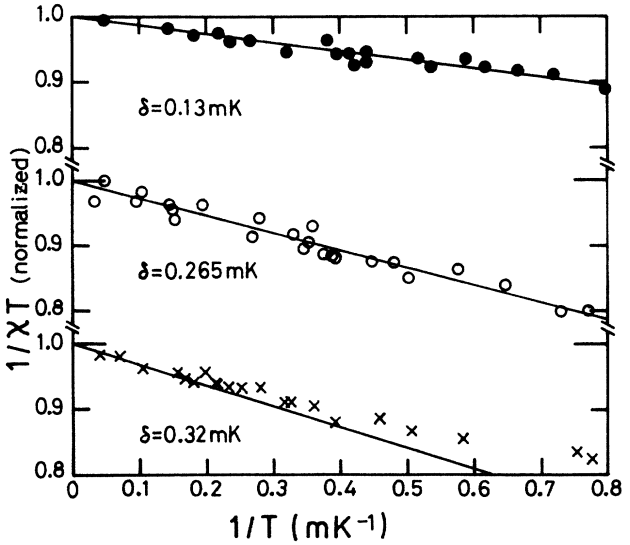

FIG. 1. Measurements of the nuclear magnetic susceptibility χ of platinum powder over a range of melting-curve temperatures T are plotted as $1/\chi T$ vs $1/T$ to determine the Weiss constant δ from the Curie-Weiss law $\chi=C/(T-\delta)$. The data are normalized to $C=1$ and shown for the Larmor frequencies 62.5 (x), 125 (○), and 250 kHz (●), corrresponding to magnetic fields of 6.8, 13.7, and 27.4 mT.

The anomalous platinum susceptibility, which appears to be a feature common to all the platinum samples discussed here, with the exception of that at Orsay,[14] also affects the value of the Curie-Weiss Δ deduced for LCMN samples. In a common calibration procedure the form $\chi_{\rm LCMN}\propto(T-\Delta)^{-1}$ is assumed and Δ is determined by comparing the LCMN susceptibility and platinum susceptibility (usually at 250 kHz) in the same cryostat, or if a platinum sample is unavailable, by measuring the LCMN susceptibility as a function of T_c at various pressures. The assumption of Curie's law for the platinum results in the attribution of a Δ to the LCMN of, for example, -0.12 mK for a sample at Helsinki[1] and -0.14 mK for a Cornell sample.[15] Our result ($\delta=0.13$ mK at 250 kHz) suggests on the contrary that $\Delta=0$ within experimental error. This contention is further supported by the recent measurements of Parpia *et al.*[2] in which the values of $\chi_{\rm LCMN}$ at T_c as a function of pressure imply $\Delta=0$ if the T_c values of Greywall[9] are used.

There is no evidence for anomalies in the susceptibility of high purity (99.999%) platinum wires[16,17] down to 48 μK. The intrinsic spin-spin interaction mechanisms in platinum, dipolar coupling, and indirect exchange, are indeed far too weak to explain a δ of the measured order of magnitude. This suggests that the ferromagnetic tendency is associated with the powder nature of the specimen or the higher level of impurities present, with the conduction electrons playing an important role.

It has been known for some time that not all samples of platinum powder are useful as ultralow temperature thermometers.[18] They are usually characterized in terms of their spin-lattice (T_1) and spin (T_2) relaxation times. We now discuss the behavior of T_2 and T_1 to establish the pedigree of our sample. The field dependence of T_2^* has been measured by recording a 2 ms sample of the free-induction decay. The decay is described by a single exponential with $T_2^*=0.83$, 1.08, 1.21 ms at 250, 125, and 62.5 kHz, respectively. These results are consistent with an intrinsic $T_2=1.5\pm0.05$ ms together with an inhomogeneous broadening proportional to applied field. This value of T_2 is somewhat larger than the 1.05 ± 0.1 ms at 20 mK previously reported.[19] The temperature dependence of T_1 has been measured at 62.5 and 125 kHz (Fig. 2) and the results are qualitatively similar to those of Avenel, Berglund, and Varoquaux.[20] A proposed explanation[21] of the deviation from a simple Korringa relation $T_1T=$ const is in terms of the formation of a Kondo state for manganese impurities (assumed noninteracting) in the platinum. The mechanism is a shift in the conduction-electron density of states at the Fermi energy, which the authors calculate as a function of applied field and which is suppressed in large fields. Our observed shift in T_1T is smaller than that reported by Avenel *et al.*[20] and would indicate a lower level of active impurities. In contrast, measurements on the Helsinki sample of platinum powder by Veuro[22] at 125 and 250 kHz give a field-dependent, but temperature-independent, Korringa constant, if Curie's law is assumed. The increase in T_1 we observed at the lowest temperatures at 125 kHz may result from eddy current heating of the powder, although the measured curves all exhibited exponential recovery. We note

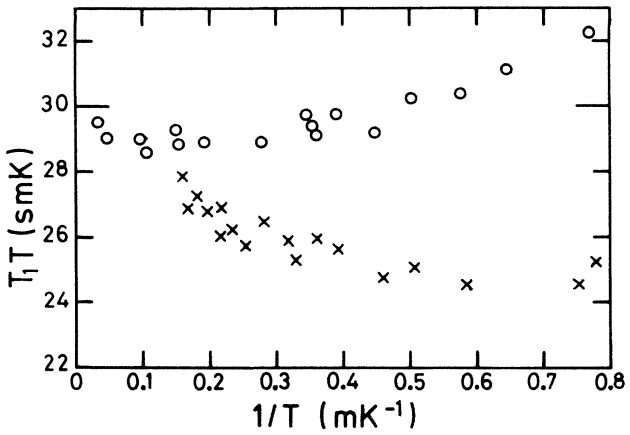

FIG. 2. Determination of the temperature dependence of the Korringa constant T_1T (smK) at Larmor frequencies of 62.5 (×) and 125 (○) kHz.

that the measured values of T_1/χ at 125 kHz systematically decrease by only 5% from 10 to 1.25 mK despite the observed deviations from the Korringa relation and Curie's law.

It follows from the result presented here that reduced temperatures ($t = T/T_c$) in superfluid ^{3}He inferred from thermometry based on assuming Curie's law for the nuclear magnetic susceptibility of platinum powder are in error, with $(1-t)$ to be scaled by $1-(\delta/T_c)$. There is a direct relation between the reduced temperature scale and the value of T_c deduced from ultrasonic spectroscopy in superfluid ^{3}He-B. In our measurements of the temperature dependence of the ultrasonic attenuation[23] we observed a B-phase collective mode for which, in the limit of zero applied magnetic field, $h\nu = 2\Delta_{sfl}$, where $2\Delta_{sfl}$ is the superfluid energy gap. At low pressures, where strong coupling corrections to the BCS energy-gap parameter $\Delta_{sfl}(T=0) = 1.764 k_B T_c$ are small, we were able to infer T_c from the *reduced temperature* of the absorption feature and the measuring frequency. Using platinum thermometry at 125 kHz, and with our original assumption of Curie's law, the T_c values were significantly smaller than those on both the Helsinki[1] and Greywall[9] scales in the pressure region explored (1.4–3.3 bars). The discrepancy with the Helsinki scale ranged from 100–140 μK while that with the Greywall scale was approximately 130 μK. Reinterpreting our results in the light of the platinum δ measured here, we find a "spectroscopic" T_c that agrees with the T_c values of Greywall to within 10 μK.

In conclusion, we have demonstrated that long standing discrepancies between platinum thermometry and other secondary thermometry at ultralow temperatures arise from anomalies in the nuclear magnetic susceptibility of platinum powder. We consider it essential that all data on superfluid ^{3}He with reduced temperatures based directly or indirectly on the assumption of Curie's law for platinum powder should be reexamined. Our recalculations have removed a large discrepancy between T_c determined spectroscopically and that measured with a melting-curve thermometer. We believe that our measurements of the deviation of the nuclear magnetic susceptibility of platinum powder from Curie's law show how the results of various groups can be reconciled to a common temperature scale. Improved accuracy in the determination of T_A remains an outstanding problem.

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[10] At 62.5-kHz quadratic fit parameters are

$$(\chi T)^{-1} = 1 - (0.317 \pm 0.029) T^{-1} + (0.123 \pm 0.034) T^{-2}$$

and the linear fit parameters are $(\chi T)^{-1} = 1 - (0.219 \pm 0.010) T^{-1}$. The rms deviations are, respectively, 0.007 and 0.009 so that further data at temperatures below 2 mK are needed to confirm the deviations from linearity we have found.

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