Nuclear magnetism in enriched $^{195}$Pt metal

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Abstract. Platinum represents both a most interesting system for study nuclear magnetism and the only standard sample of NMR thermometry at ultra-low temperatures. Magnetization, specific heat and nuclear magnetic resonance measurements were performed in a 93.52% enriched $^{195}$Pt metal with an iron concentration of 105 ppm. Both nuclear magnetic resonance and relaxation are strongly influenced by the 3d-impurities.

1. Introduction
Platinum has become the standard sample of nuclear magnetic resonance (NMR) thermometry at ultra-low temperatures because of some attractive nuclear magnetic properties. The only magnetic isotope in platinum is $^{195}$Pt with the natural abundance of 34%. It has a nuclear spin $I = \frac{1}{2}$ which excludes any quadrupolar effects. Both the absence of quadrupolar effects and the dominant indirect exchange coupling between nuclear spins reduce the NMR linewidth and make it practically ideal Lorentzian. Moreover, the spin-lattice relaxation time $\tau_1 = K/T_e$ for establishing thermal equilibrium between the electronic system at temperature $T_e$ and the nuclear spin system is short. The Korringa constant of platinum has the very small value $K = 30$ mKs. A further useful property of platinum is its long spin-spin relaxation time of $\tau_2 = 1.2$ ms, simplifying signal detection.

Accurate Pt NMR thermometry at ultra-low temperatures, however, is limited by a possible magnetic ordering of the exchange-dominated nuclear spin system and the strong influence of electronic magnetic impurities on the nuclear magnetism in platinum. An approximate estimate of the possible nuclear magnetic ordering temperature $T_c$ of isotopically pure $^{195}$Pt yields 1 µK [1]. Thus it should be possible to observe nuclear magnetic ordering of $^{195}$Pt at a temperature of nuclear spins in a state of equilibrium with the conduction electrons. For natural platinum the ordering temperature is expected to be below 0.35 µK, because $T_c$ is proportional to the number of next-nearest neighbors of magnetic isotopes. Yet it is not clear whether the $^{195}$Pt nuclei undergo a phase transition to a long-range ordered state or remain in some metastable magnetic state.

In order to investigate nuclear magnetism in platinum and to study the dependency of the nuclear relaxation on 3d-impurities, magnetization, specific heat and NMR measurements were performed in enriched $^{195}$Pt metal with an iron concentration of 105 ppm.

2. Experimental results

2.1. Sample
The sample produced by the Oak Ridge National Laboratory (ORNL) was a (93.52 ± 0.14)% enriched $^{195}$Pt rod of 2 mm diameter and 10 mm length. The content of the other non-magnetic isotopes $^{194}$Pt, $^{193}$Pt,
\(^{196}\)Pt, \(^{198}\)Pt and \(^{192}\)Pt was determined to be 3.51 ± 0.16, 2.75 ± 0.08, 0.19 ± 0.01 and 0.02 ± 0.01 atomic percent, respectively. Whereas the spectrographic analysis (SSMS) showed rather low concentrations of magnetic impurities such as nickel, manganese and cobalt (Ni:3.0 ppm, Mn:2.0 ppm, Co:0.02 ppm), the iron concentration was identified to be \(c_{Fe} = 105\) ppm. This resulted in a residual resistivity ratio (RRR) of 47±4, which was measured by the eddy-current method. After annealing the \(^{195}\)Pt rod at 1000 °C for 60 hours in vacuum \((p = 10^{-6}\) mbar\), the RRR was increased to 100±6.

2.2. Static magnetization

Magnetization measurements of a 51 mg sample, cut from the \(^{195}\)Pt rod, were performed by means of a commercial SQUID magnetometer (MPMS-5T, Quantum Design) at 1.9 K \(\leq T \leq 300\) K and in a field of magnetic induction \(B = (0,0,B) = 1\) T. The magnetic moment \(m = (0,0,m)\) can be described by

\[
m = \frac{c_{Fe} N_A J g \mu_B V}{V_m} B_f(x),
\]

where \(m_{sat} = c_{Fe} N_A J g \mu_B V / V_m\) is the saturation magnetic moment, and \(B_f(x)\) is the Brillouin function for the angular momentum quantum number \(J\) with the argument \(x = J g \mu_B B / kT\). Here \(g\), \(\mu_B\), \(k\), and \(N_A\) represent the electronic Landé factor, Bohr’s magneton, Boltzmann’s constant and Avogadro’s number respectively. The saturation magnetic moment of the sample with volume \(V = 2.378 \times 10^{-3}\) cm\(^3\) and molar volume \(V_m = 9.09\) cm\(^3\)/mol was determined to be \(m_{sat} = 1.303 \times 10^{-6}\) Am\(^2\). The best fit to the measured data using equation (1) was obtained for an iron concentration of \(c_{Fe} = (105 ± 4)\) ppm with an effective moment \(J g \mu_B = (8.5 ± 0.3)\mu_B\). It was reconfirmed that \(J\) tends to infinity as \(g\) gets close to zero. This means that the iron impurities in platinum polarise the conduction electrons, resulting in so-called giant moments with respect to their value and spatial extension [2,3]. In the high-temperature approximation \((x << 1)\), the magnetization depends inversely on temperature according to Curie’s law with a Curie constant of \(C = 1.312\) mK.

2.3. Specific heat

In this experiment, the same sample was used as for the magnetization measurement. Specific heat was determined in the temperature range 0.35 K \(\leq T \leq 30\) K and in magnetic fields up to 8 T by a commercial relaxation type calorimeter (MagLab\(^{19}\) microcalorimeter, Oxford Instruments). The total observed specific heat can be attributed to the sum of contributions from electrons, phonons, iron impurities, and nuclear magnetic moments,

\[
c(T, B) = \gamma T + \beta T^3 + \frac{c_{Fe} n_B k}{\rho} x^2 \frac{dB_f(x)}{dx} + \frac{n_{Pt195} k}{\rho} y^2 \frac{dB_f(y)}{dy},
\]

By least-squares fit the electronic specific-heat coefficient was obtained to be \(\gamma = 33.28 ± 0.02\) μJ/K\(^2\)g, in agreement with data reported in [4]. The Debye coefficient in equation (2) was determined to be \(\beta = 0.768 ± 0.003\) μJ/K\(^4\)g, corresponding to a Debye temperature of \(\Theta_B = 235\) K. This value should agree with the Debye temperature calculated from the elastic constants in the low-temperature limit which is 237.8 ± 1.5 K [5]. The third term in equation (2) represents the magnetic contribution from the iron impurities with concentration \(c_{Fe} = 105\) ppm. Here \(n_B = 6.62781 \times 10^{23}\) m\(^{-3}\) the number density of platinum atoms, and \(\rho = 21.47 \times 10^6\) gm\(^{-3}\) is the mass density of platinum. In contrast to the magnetization measurement, however, the analysis of the specific heat data resulted in the small quantum number \(J = 2\) and the electronic Landé factor \(g = 2\). The discrepancy between the results for the angular momentum quantum number, as obtained from the specific heat and those from the magnetization measurement, can be resolved by considering the giant moment as a dynamical magnetic unit [2]. At last, the nuclear specific heat is represented by the last term in equation (2). Here
\( n_{Pt}^{195} = 0.9352 \times n_{Pt} \) is the number density of the magnetic isotope \(^{195}\text{Pt} \), and \( B(y) \) is the Brillouin function for nuclear spin \( I = \frac{1}{2} \) with the argument \( y = I_g \mu_B B / kT \). The nuclear magnetic moment of \(^{195}\text{Pt} \) is given by \( I_g \mu_N = 0.597 \mu_N \), where \( \mu_N \) is the nuclear magneton.

2.4. Nuclear magnetic resonance

Pulsed NMR measurements were performed on the 93.52% enriched \(^{195}\text{Pt} \) rod at ultra-low temperatures. The platinum rod was screwed horizontally into a silver sample holder, which was attached to the copper nuclear stage of the microkelvin cryostat [6]. The RF coil is made by wrapping 900 turns of copper wire of 20 \( \mu \)m diameter around the platinum sample. Static field coil and shields were mechanically and thermally anchored to the mixing chamber of the dilution refrigerator only. In order to investigate the influence of the \(^{195}\text{Pt} \) concentration and the iron impurities on the nuclear magnetic properties in platinum, the experimental set-up to study NMR in enriched \(^{195}\text{Pt} \) metal was identical to that of the Pt-NMR thermometer located at the top of the copper stage too. The sample used in the Pt-NMR thermometer was made from a high-purity platinum rod with an iron concentration of \( c_{Fe} < 5 \) ppm. Pulsed NMR in high-purity natural platinum was established to be the only method available at present for reliable thermometry down to 20 \( \mu \)K [6,7].

For the NMR measurements a RF frequency of \( f = 250 \) kHz was used, corresponding to a magnetic field of \( B = 28.5 \) mT. Based on a gyromagnetic ratio of the bare nucleus of \( \gamma / 2\pi = 9.094 \) kHz/mT, the Knight shift was obtained to be -3.54% for both natural and enriched platinum metal.

The signal amplitude of the free induction decay (FID) induced by a \( \pi/2 \) pulse was severely reduced for the enriched \(^{195}\text{Pt} \) in comparison to that for high-purity natural platinum. The resonance line, however, is inferred from the FID was observed to be very Lorentzian. In figure 1 the magnitude of the Fourier transform of the FID measured for several magnetic fields at a temperature of 8.7 mK is shown.

![Figure 1](image)

**Figure 1.** Fourier transform of the FID measured for magnetic fields \( 27.9 \) mT \( \leq B \leq 29.1 \) mT at 8.7 mK. The left graphic shows a 3D plot of the magnitude \( M(\omega = 2\pi f, B) \). The right graphic is a contour plot, clearly representing the frequency shift due to the magnetic field.

The decay time \( \tau_2^* \) results for a single Lorentzian line from the full width at half height of \( 2/ \tau_2^* \). It was determined to be \((140 \pm 20) \) \( \mu \)s at 8.7 mK and remains nearly constant to lower temperatures down to 200 \( \mu \)K. Assuming a separation of the relaxation rate \( \tau_2^{-1} \) into an intrinsic part \( \tau_{195Pt}^{-1} \) and a part caused by the iron impurities, \( \tau_{Fe}^{-1} \propto B_J (x) \), the intrinsic spin-spin relaxation time of enriched \(^{195}\text{Pt} \) can be identified from the increase of \( \tau_2^* \) for \( T > 10 \) mK. It was found that \( \tau_{195Pt} \) is \((770 \pm 20) \) \( \mu \)s and the...
temperature dependent part of the relaxation rate \( \tau_{\text{Fe}}^{-1} \) at \( B = 28.5 \text{ mT} \) follows a Brillouin function with \( J \gg 100 \) and a giant moment of \( 8.5 \mu_B \). This is consistent with the results obtained in the magnetization measurement.

The spin-lattice relaxation time of the enriched \( ^{195}\text{Pt} \) sample was measured by a three-point method in the magnetic field of 28.5 mT. In this magnetic field, the Korringa constant was determined to be \( K = (17 \pm 5) \text{ mKs} \). It is assumed that the strong interaction between the magnetic moments of the iron impurities and the nuclei is responsible for the decrease of \( K \) [3]. With increasing magnetic field, however, the Korringa constant of enriched \( ^{195}\text{Pt} \) could approach the value of pure platinum [8].

The longitudinal magnetization \( M_0 \) obtained from pulsed NMR measurements at the external magnetic field \( H_0 \) did not obey the Curie-Weiss law, \( M_0 \propto 1/(T - \Theta) \). This is attributed to the iron impurities which alter the relation between external field \( H_0 \) and internal field \( B \). Then, the longitudinal magnetization depends on content and nature of the impurity moment, and on the unknown temperature \( T_e \) of the electronic system after the tipping pulse [7]. For that reason, the Weiss temperature \( \Theta \) of enriched \( ^{195}\text{Pt} \) could not be determined.

3. Conclusion
Dissolved 3d-impurities like iron polarise the conduction electrons in platinum and form giant moments. Both nuclear magnetic resonance and relaxation in \( ^{195}\text{Pt} \) metal are strongly influenced by the iron impurities. The NMR signal is reduced because nuclear magnetic moments near to a giant moment are completely wiped out from resonance. Moreover, the longitudinal magnetization depends on content and nature of the impurity moment, and on the temperature of the electronic system after the tipping pulse. This results in deviations from the Curie-Weiss law.

The reduced intrinsic spin-spin relaxation time in 93.52% enriched \( ^{195}\text{Pt} \) metal was determined to be 770 \( \mu\text{s} \). The observed decay time \( \tau_2^* = 140 \mu\text{s} \) remains constant below the spin glass freezing temperature of the giant moments at 10 mK [9]. Above 10 mK the decay time depends on temperature. No frequency shift or line splitting of the Lorentzian resonance line was observed in the temperature range \( 200 \mu\text{K} \leq T \leq 10 \text{ mK} \).

We are currently examining high-purity enriched \( ^{195}\text{Pt} \) metal to search for a nuclear magnetic ordering at accessible electron temperatures \( T < 10 \mu\text{K} \).

Acknowledgments
I gratefully acknowledge the contributions of M. Meißner and K. Kiefer from HMI Berlin to the measurements of specific heat and magnetization.

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