Electronic and Nuclear Magnetism in Platinum-Iron at Ultralow Temperatures

LOW TEMPERATURE WORLD RECORD ESTABLISHED

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In February, 1996, physicists at the University of Bayreuth claimed a world record for producing the lowest temperature yet achieved when they announced the results of their work with platinum. They cooled 31.4 grams of platinum to 2 millionths of a degree Celsius above absolute zero temperature, −273.15°C. In this paper they describe the theory and the practical work behind this accomplishment. Research in low temperature physics involves the construction of detailed and precise knowledge of the atomic and nuclear structures and their interactions in atoms. Some effects due to atomic and nuclear structure, particularly magnetic effects, are only seen at very low temperatures; however their effects have consequences at higher temperatures, although these are not usually observed. Thus, this and other low temperature work is contributing to a fundamental understanding of the magnetic behaviour of materials.

The study of magnetism is one of the most interesting fields in solid state physics. Electronic magnetism shows a wide spectrum of different ordering phenomena at temperatures from about 10^3 K, where the ferromagnetic phase transition in iron occurs, to about 10^{-3} K, where Ce^{3+} ions in the paramagnetic salt CMN order magnetically. (CMN is cerium magnesium nitrate, $2Ce^{3+}(NO_3)_3·3Mg(NO_3)_2·24H_2O$, which previously found application for electronic demagnetisation refrigeration before ^3He-^4He dilution refrigerators were used (1). Nowadays some research groups use it for thermometry at mK temperatures, but we used a PdFe thermometer in this temperature range).

Interacting magnetic moments of localised electronic shells or itinerant electrons are responsible for phenomena such as ferro-, ferri-, anti-ferro- and meta-magnetism or spin glass freezing. However, many elements and compounds do not contain such underlined electronic magnetic moments, but very often their nuclei carry a magnetic moment due to the nuclear spin. Since nuclear magnetic moments are three orders of magnitude smaller than their electronic counterparts, and as the interaction energy is proportional to the square of the magnetic moment, ordering phenomena in the nuclear spin system are expected to occur only in the microkelvin temperature range or at even lower temperatures.

Apart from solid ^3He with its strong quantum-mechanical direct exchange force, and the Van Vleck paramagnets with hyperfine enhanced magnetic moments, one has to distinguish between two groups of nuclear spin systems:

- those in insulators and metals with a weak coupling between the nuclei and the conduction electrons, and
- those in metals with a strong coupling between the nuclei and the conduction electrons.

The Korringa constant, κ, is an important parameter to characterise the strength of this interaction. The Korringa constant is given by the conduction electron temperature, $T_{electron}$,

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multiplied by the spin lattice relaxation time, τ_1.

For the first group of materials, the Korringa constant is larger than 1 Ks. As the spin lattice relaxation time τ_1 becomes very long at temperatures below 1 mK ($\tau_1 > 1000$ s), it is possible to cool only the nuclear spin system to nanokelvin or even picokelvin temperatures for a time long enough to perform nuclear magnetic investigations, while the conduction electrons stay at a much higher temperature ($T_{electron} > 100 \mu K$). For systems such as these, nuclear magnetic ordering phenomena have been observed in silver ($\kappa = 12$ Ks, $T_c = 0.6$ nK) and copper ($\kappa = 1.3$ Ks, $T_c = 60$ nK) (2).

However, it is much more difficult to observe nuclear magnetic ordering phenomena in the second group, since in this case, the whole system has to be cooled because of the strong coupling between the electrons and the nuclei. On the other hand the indirect exchange interaction between nuclei in these systems is stronger than the dipole-dipole interaction, and therefore ordering phenomena are expected to occur at temperatures of up to tens of microkelvin.

Work with Platinum as a Strong Coupling System

Recently, we have been able to observe a nuclear ferromagnetic transition of this type with the ^{113,115}In nuclei in AuIn$_2$ ($\kappa = 0.11$ Ks) at a temperature of 35 μK (3). Another very interesting material in this group is platinum, which has a very small Korringa constant, of size only $\kappa \leq 0.03$ Ks. The nuclear magnetic moment of ^{195}Pt is a factor of 10 smaller than that of the indium nuclei and only 33.8 per cent of the platinum nuclei carry the rather small magnetic moment of 0.597 μ_n (nuclear magneton $\mu_n = 5.05 \times 10^{-27}$ Am^2). Therefore, it is necessary to reach temperatures below 1 μK to observe nuclear magnetic ordering in platinum (4).

The additional interest in platinum comes from the fact that <u>electronic</u> magnetic $3d$ impurities, such as iron, form so-called giant moments in this strongly enhanced electronic Pauli paramagnet. (Platinum and also palladium are both strongly exchange enhanced Pauli paramagnets.) The giant moments show spin glass freezing at

temperatures of a few mK at concentrations of ppm (5). This system of randomly distributed electronic magnetic moments may have a strong influence on the nuclear magnetic properties.

Searching for Nuclear Magnetic Ordering in Platinum

In order to search for a possible nuclear magnetic ordering of ^{195}Pt and to study the above mentioned interaction between nuclear and electronic magnetism, we have investigated platinum samples containing magnetic impurities at concentrations of 11 and 41 ppm. The impurities were mainly iron, carrying an electronic magnetic "giant" moment of eight times the Bohr magneton μ_B ($\mu_B = 9.274 \times 10^{-24}$ Am^2). The properties that we measured were:

- heat capacity in magnetic fields, B; (0 ± 0.05) mT $\leq$ B $\leq$ 248 mT
- AC susceptibility at B = (0 ± 0.05) mT and
- nuclear magnetic resonance at fields 2.5 mT $\leq$ B $\leq$ 22.8 mT.

Measurements were taken at temperatures $T_{nuclear} \geq 0.3 \mu K$ and $T_{electron} \geq 2 \mu K$, the latter being the lowest temperature to which electrons and phonons of a material have ever been refrigerated.

Lowering the Platinum Temperature

The ultralow temperatures that are necessary for these experiments were obtained by using the adiabatic nuclear demagnetisation technique. First, 17 kg copper were precooled in the Bayreuth nuclear demagnetisation refrigerator (6) (6.5 kg in an external field of 8 T) by a commercial ^{3}He-^{4}He dilution refrigerator to a temperature of 11 mK.

Then, after a thermal decoupling of the copper nuclear refrigeration stage from the mixing chamber of the dilution refrigerator, the external magnetic field was slowly reduced. At the end of this process the copper stage reached temperatures of about 50 μK. The platinum sample (n = 161 mmole of weight 31.4 grams) was exposed to a magnetic field of 0.37 T and thermally connected to the copper stage via a superconducting aluminium heat switch. The platinum was then precooled, by the copper stage, to a temperature of approximately 100 μK.
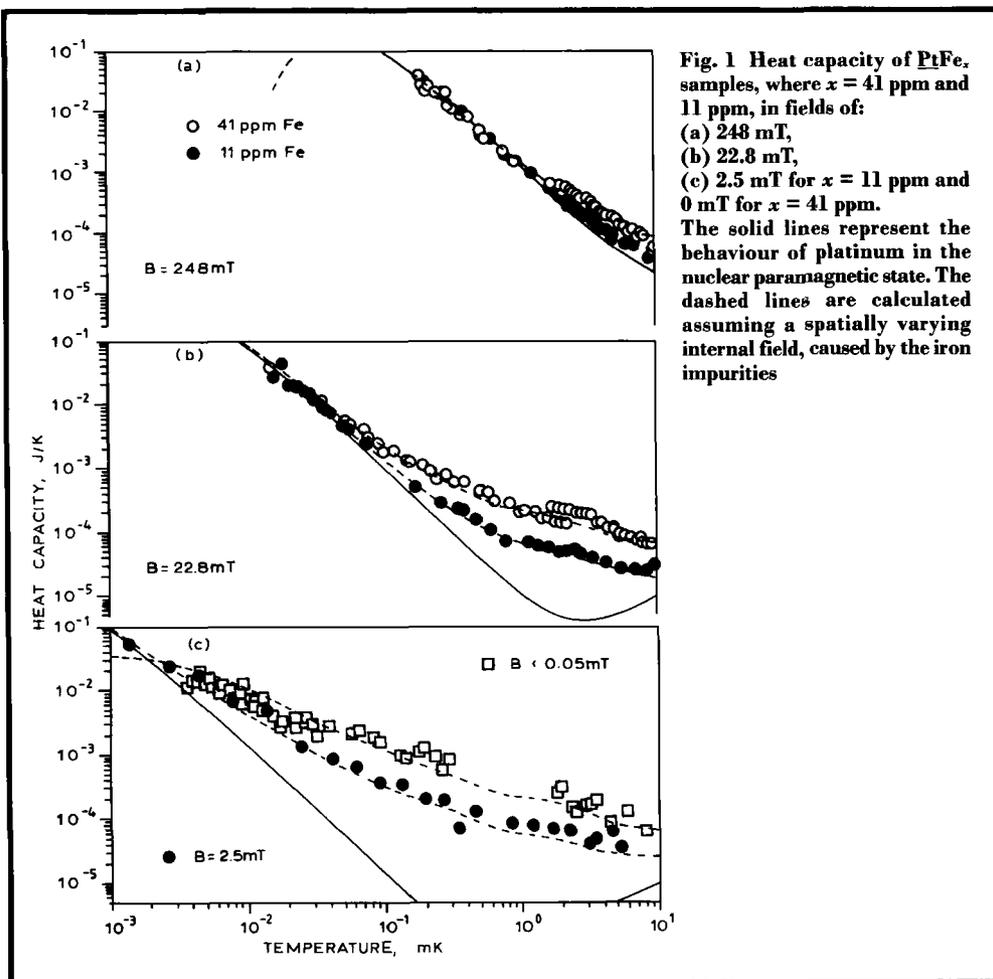
Fig. 1 Heat capacity of PtFe$_x$ samples, where $x = 41$ ppm and 11 ppm, in fields of:
(a) 248 mT,
(b) 22.8 mT,
(c) 2.5 mT for $x = 11$ ppm and 0 mT for $x = 41$ ppm.
The solid lines represent the behaviour of platinum in the nuclear paramagnetic state. The dashed lines are calculated assuming a spatially varying internal field, caused by the iron impurities

Subsequently, the platinum stage was thermally decoupled from the copper stage and the field was reduced. Eventually, in external fields of $B \leq 0.05$ mT, the temperature of the nuclear spin system of platinum reached 0.3 µK. In these fields ($B \leq 0.05$ mT) the temperature of the nuclei, $T_{nuclear}$, was lower than the temperature of the conduction electrons, $T_{electron}$.
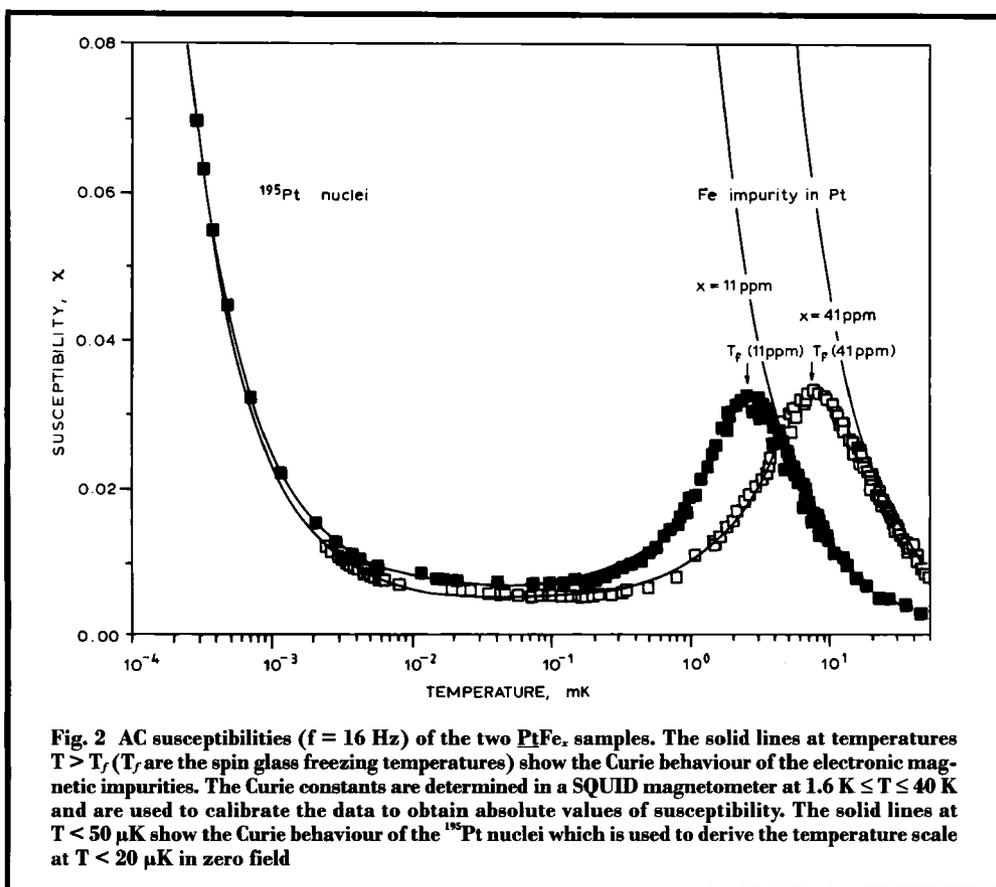
If the adiabatic demagnetisation was stopped at somewhat higher fields, for example 2.5 mT, nuclear temperatures of (0.8 ± 0.2) µK could be measured directly after demagnetisation. Taking the measured heat leak of (12 ± 2) pW into the platinum sample into account and the measured Korringa constant $\kappa = (7 \pm 3)$ mKs for platinum in these fields, the temperature of

the conduction electrons has to be below 2 µK.

During the next three hours after finishing the demagnetisation the conduction electrons stayed below 3 µK. The small value of 7 mKs for the Korringa constant, in contrast to its literature value of 30 mKs, is caused by magnetic impurities.

Measurement of the Platinum Temperature

The temperature of the platinum was determined from the magnetisation of its nuclear spin system, using pulsed nuclear magnetic resonance (NMR) in fields $B \geq 2.5$ mT and the AC susceptibility technique in fields $B = (0 \pm 0.05)$ mT. At temperatures of ≥ 20 µK the NMR signal was calibrated against an independent platinum-wire-NMR thermometer, which is itself calibrated

Fig. 2 AC susceptibilities (f = 16 Hz) of the two PtFe$_x$ samples. The solid lines at temperatures T > T$_f$ (T$_f$ are the spin glass freezing temperatures) show the Curie behaviour of the electronic magnetic impurities. The Curie constants are determined in a SQUID magnetometer at 1.6 K ≤ T ≤ 40 K and are used to calibrate the data to obtain absolute values of susceptibility. The solid lines at T < 50 μK show the Curie behaviour of the ^{195}Pt nuclei which is used to derive the temperature scale at T < 20 μK in zero field

against the paramagnetic susceptibility of a PdFe$_x$ sample at temperatures T ≥ 10 mK (1).

For the temperature calibration we assume that the magnetisation, detected by the NMR signal and the measurement of nuclear AC susceptibility, follows a Curie law ($\chi \sim 1/T_{nuclear}$) at low polarisation. If it follows a Curie-Weiss law ($\chi \sim 1/(T_{nuclear} - \Theta_n)$), we would have to correct our temperature scale by Θ_n (see below).

The measured heat capacity data of the two PtFe$_x$ samples in different magnetic fields is shown in Figure 1. The solid lines show the nuclear paramagnetic behaviour. In a magnetic field of 248 mT, there is a good agreement at T ≤ 1 mK. However, at higher temperatures the measured heat capacities are larger than expected and scale with the impurity concentration. At lower fields, such as 22.8 mT, this effect is much more pronounced, and at 2.5 mT or in zero field

we observe an enhanced heat capacity over almost the whole temperature range. This effect can be described by a spatially varying internal field caused by the electronic magnetic impurities, assuming that this field behaves in a similar way to the electronic polarisation cloud in the conduction electron system – which forms the giant electronic moment. The dashed lines in Figure 1 are calculated using only two fitting parameters. There is a good agreement with the measured data. Therefore, we are able to describe the internal field in platinum as being due to electronic magnetic impurities.

Does Platinum Have Nuclear Magnetic Ordering?

In order to search for a nuclear magnetic ordering transition in platinum, we have measured the nuclear and electronic AC susceptibilities

of the two platinum samples in an external field $B \leq 0.05$ mT. The results are shown in Figure 2. The two maxima at millikelvin temperatures are caused by the "spin glass freezing" of the magnetic $3d$ impurities in platinum at freezing temperature, T_f. At temperatures $T > T_f$ the AC susceptibility shows Curie behaviour with Curie constants $C_{11ppm} = 122$ µK and $C_{41ppm} = 448$ µK, determined at $1.6 \leq T \leq 40$ K in a commercial SQUID magnetometer.

We used this known behaviour (5) to scale our measured data in units of differential volume susceptibility. At $T < T_f$ the susceptibility decreases linearly with temperature and increases again at $T < 0.1$ mK. The latter increase is caused by the nuclear paramagnetic behaviour of the ^{195}Pt nuclei with a Curie constant of $C_{Pt} = 0.0185$ µK. No maximum in the susceptibility was found and therefore no evidence for nuclear ordering in our samples could be detected down to the minimum nuclear temperature reached of 0.3 µK.

Conclusions

The temperatures achieved in our platinum samples, for the conduction electrons and phonons, which are below 2 µK, are the lowest temperatures ever reached in equilibrium. No evidence of nuclear magnetic ordering in platinum could be detected. This shows that the temperatures achieved were still measured in the nuclear paramagnetic state where the Curie (or Curie-Weiss) law is valid, and therefore our determination of temperature, assessed via this law is correct.

This work should aid in extending understanding of the interplay between electronic and nuclear magnetism at very low temperatures.

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Palladium Colloid Catalyst Used in Microcontact Printing

There are several methods in current use for transferring very fine patterns onto substrates for printed electronic circuitry. These all involve the selective metallisation of the area to be treated and use various techniques, such as photolithography or electroless plating. However, scientists at Harvard University have now announced a new method of electroless deposition, which they have demonstrated with copper but suggest could also be used for the deposition of other metals (P. C. Hidber, W. Helbig, E. Kim and G. M. Whitesides, "Microcontact Printing of Palladium Colloids: Micron-Scale Patterning by Electroless Deposition of Copper", *Langmuir*, 1996, 12, (5), 1375–1380).

Their new strategy involves the manual transfer of a palladium colloid catalyst onto a substrate surface by microcontact printing (µCP); this uses a patterned elastomer stamp made from poly(dimethylsiloxane). The stamp is previously dipped into the palladium colloid, which has been stabilised with tetraalkylammonium bromides. This is followed by the electroless deposition of copper which proceeds by immersion of the substrate in a copper plating bath, and occurs only at the regions coated with the palladium colloid, where a catalytic reaction occurs.

Copper lines of micron and submicron widths, having edge resolution of 100 nm, were produced on a variety of substrates, including glass, silicon with a silicon dioxide layer, and polymers. Both flat and curved surfaces can be plated without loss of resolution. In addition, freestanding, flexible structures can be produced by dissolving the substrate when the metal film reaches the required thickness or by allowing the internal stress in the electroless copper layer to exceed the adhesion strength, when delamination occurs.

While films of approximately uniform thickness can be produced by this method, ways of obtaining structures which have different layer thicknesses have also been developed.