Superconductivity of Compacted Platinum Powder at Very Low Temperatures

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We report the observation of superconductivity in compacted, high purity platinum powder of average grain size $\approx 2\ \mu$m. The transition into the superconducting state was found by measuring resistivity and ac susceptibility as well as dc magnetization. The transition temperature T_C strongly depends on the compression of the powder; we found $0.62 \leq T_C \leq 1.38$ mK for packing fractions of $0.8 \geq f \geq 0.5$, respectively. The corresponding critical magnetic fields are $6.6 \leq B_C(0) \leq 67\ \mu$T. [S0031-9007(99)09231-5]

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As early as the middle of the 1970s, the number of metallic elements in which superconductivity had been detected had far surpassed the number of nonsuperconducting metals. At that time there already was speculation that, apart from a few mono- or divalent metals, superconductivity might well be observed in all the nonsuperconducting metallic elements, if they could just be cooled to low enough temperatures [1]. To this day, the element of the periodic table with the lowest transition temperature into the superconducting state is rhodium with $T_C = 325\ \mu$K [2]. Despite considerable efforts, none of the remaining metallic elements among the alkali, the alkaline earth, and the noble metals (Cu, Ag, Au), as well as platinum and palladium, revealed any indication of superconductivity, although the accessible temperature range has been extended down to an equilibrium temperature of a few microkelvins during the past decade [3]. The purity of the materials, especially with regard to the concentration of *magnetic* impurities, is considered to be the most important obstacle to a possible superconducting transition in those elements.

One of the most interesting candidates among these metals is the fcc metal platinum. Its strong electron-phonon coupling is expected to favor the formation of Cooper pairs and thus superconductivity. On the other hand, its strong electron-electron exchange interaction and the resulting enhancement of its paramagnetic Pauli susceptibility brings this metal close to a ferromagnetic instability. Among the metals which do not show magnetic ordering, platinum has one of the largest exchange enhanced Pauli susceptibilities, $\chi_{\mathrm{exp}}(T \rightarrow 0) = S\chi_{\mathrm{Pauli}}$, with a Stoner enhancement factor $S = 3.9$ [4]. As a consequence, the $5d$ conduction electrons of platinum show strong spin fluctuations on short length and time scales which will tend to suppress the superconducting transition [5].

Another consequence of the large Stoner factor is an enhancement of the effective moments of magnetic $3d$ impurities (e.g., Fe, Mn, Co) in platinum due to the polarization of the neighboring $5d$ conduction electrons of the host metal [6]. The magnitude of these "giant moments" in Pt is $\mu_{\mathrm{gm}} = (8 \pm 1)\mu_B$ at a magnetic impurity concentration x of $2 \leq x \leq 100$ ppm [4]. Spin glass freezing of the giant moments in platinum was observed at freezing temperatures $T_f/x = 0.26$ mK/ppm for $5 \leq x \leq 75$ ppm [7].

In the course of recent investigations of the nuclear magnetic properties of the isotope ^{195}Pt (natural abundance 33.4%), the minimum equilibrium temperature of conduction electrons, nuclei, and lattice could be lowered to $T_{\mathrm{min}} \simeq 1.5\ \mu$K [3], without any indication of a magnetic ordering or a superconducting transition. One may conclude from these studies that the magnetic correlations in platinum seem to be of greater importance compared to the electron-phonon coupling, and thus prevent superconductivity in this metal.

The investigations on platinum reported so far were performed on *bulk* samples with dimensions of at least a few millimeters. However, our recent studies of the magnetic properties of Pt samples made of compacted platinum *powder* with a typical grain size of about $2\ \mu$m showed a magnetic behavior very different from the bulk material. Whereas the Stoner enhancement of the Pauli susceptibility of Pt at kelvin temperatures is observed in samples of the compacted powder, too, they show a much weaker temperature dependence of the dynamic susceptibility in the mK and μK temperature range measured in a superimposed static field of $B \simeq 0.1$ mT. In contrast to bulk Pt, no spin glass transition of giant moments is observed in the compacted powder, where the susceptibility of the localized magnetic impurities is reduced by more than 1 order of magnitude. In search of an explanation for this unexpected magnetic behavior, measurements in an experimental setup with a significantly improved compensation of the surrounding static field (compared to the previous studies in a noncompensated setup with $B_{\mathrm{min}} \simeq 0.1$ mT) appeared to be of particular importance.

Measurements of the magnetic properties of the compacted powder samples were performed in three different experimental setups: two susceptometers for ac-susceptibility measurements [7] and one SQUID magnetometer for dc magnetization measurements. The

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electrical resistivity of the compacted powder was investigated in a separate experiment. Each setup is surrounded by a superconducting Nb shield and is equipped with a dc-field coil which enables field compensation in the z direction of the samples, in addition to the compensation (for all spatial directions) of a Helmholtz coil system around the cryostat; we estimate the final static field at the samples to be $\simeq 1$ μT. All setups were attached to the Cu stage of a nuclear demagnetization refrigerator [8] and thermally isolated from their corresponding coil systems which were anchored to the mixing chamber of the precooling dilution refrigerator.

The cylindrical samples (diameter 5 mm, length 2–5 mm) were produced by compressing 0.5–1 g of platinum powder [9] at pressures of $1.0 \leq p \leq 4.5$ kbar resulting in packing fractions f of $0.50 \geq f \geq 0.80$, respectively. X-ray diffraction of the lattice structure of the powder at room temperature confirmed the lattice constant of bulk Pt known from literature ($a = 0.3924$ nm). The topological structure of the powder was investigated by electron microscopy, and the average size of the grains is about 2 μm [10]. We searched for possible surface impurities using Auger spectroscopy, and detected carbon and oxygen as main impurities. In dc arc emission spectroscopy as well as inductively coupled mass spectroscopy, the following four elements with a concentration >1 ppm were detected in the powder: Zn (2 ppm), Pd (3 ppm), Rh (7 ppm), and Ti (7 ppm) [11]. Additional information concerning the concentration of paramagnetic impurities in the powder was derived from studies of the temperature dependence of the magnetic moments of the samples in the kelvin temperature range at magnetic fields up to $B = 6$ T using a commercial SQUID magnetometer [12]. We found a concentration of magnetic impurities of $x = (4 \pm 1)$ ppm; however, the magnetization measurements do not allow one to address this magnetic contribution to a particular element. By comparing the results of the mass spectroscopy analysis and of the dc magnetization measurements, we conclude that there is a small amount of magnetic impurities in the powder (or on its surface), but these impurities do not necessarily belong to the group of elements (e.g., Fe, Mn) known to form giant moments in platinum. Finally, the sample characterization was completed by thermogravimetry and differential thermal analysis without any indications of an impurity phase up to a temperature of the samples of 1570 °C.

Figure 1a shows the temperature dependence of the ac susceptibility of a sample of platinum powder with a packing fraction $f = 0.67$, measured in zero field at a frequency of 16 Hz using a commercial ac susceptibility bridge [13]. All data were taken during a warm-up of the Cu nuclear stage, from its base temperature of ≈ 80 μK to 10 mK within typically ten days. In contrast to the spin glass behavior observed in bulk platinum with a small amount of magnetic impurities [7], the susceptibility of the compacted Pt powder shows hardly any temperature dependence at $100 \geq T \geq 1.5$ mK. However, at lower temperatures, the susceptibility suddenly drops to a value of $\chi \simeq -0.9$. This strong decrease in the ac susceptibility is accompanied by a distinct step in the electrical resistance of the compacted powder, from its "high" temperature value of $R = 3.8$ $\mu\Omega$ to a value which is, within experimental scatter, <100 nΩ (Fig. 1b). In Fig. 2, the temperature dependence of the dc magnetization of a sample with a smaller packing fraction ($f = 0.50$) than those whose ac susceptibility data are shown in Fig. 1 ($f = 0.67$) is presented. The change in the magnetization is caused by the exclusion of an applied static magnetic field from the sample, and is thus a confirmation of the Meissner effect in the compacted platinum powder. We conclude that the magnetic properties and the electrical resistivity show clearly a transition into the superconducting state of the investigated samples.

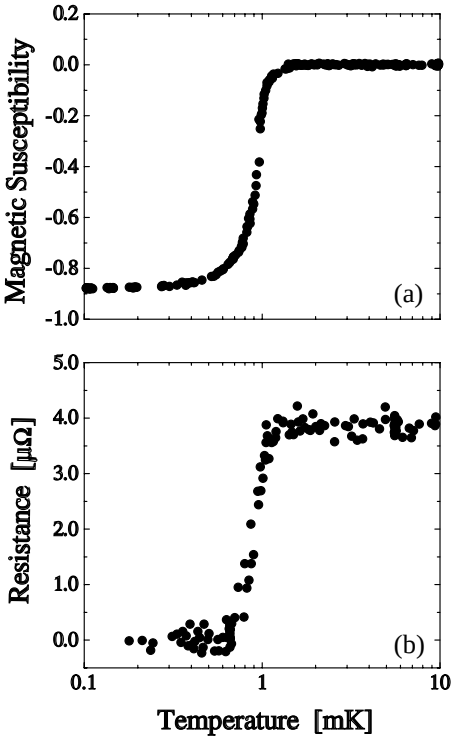

FIG. 1. (a) Temperature dependence of the ac susceptibility (in SI units) of compacted Pt powder of packing fraction $f = 0.67$ in zero magnetic field. (b) Temperature dependence of the electrical resistance of the compacted Pt powder ($f = 0.67$).

As already indicated by the data of Figs. 1 and 2, the transition temperature is strongly dependent on the packing fraction f of the powder. In the ac susceptibility setup, we have investigated samples of three different packing fractions $f = 0.50$, 0.67, and 0.80, corresponding to pressures of $p = 1.0$, 2.5, and 4.5 kbar applied to compress the powders at room temperature. These samples showed transition temperatures $T_C = 1.38$, 1.04, and 0.62 mK, respectively. Figure 3 shows that the

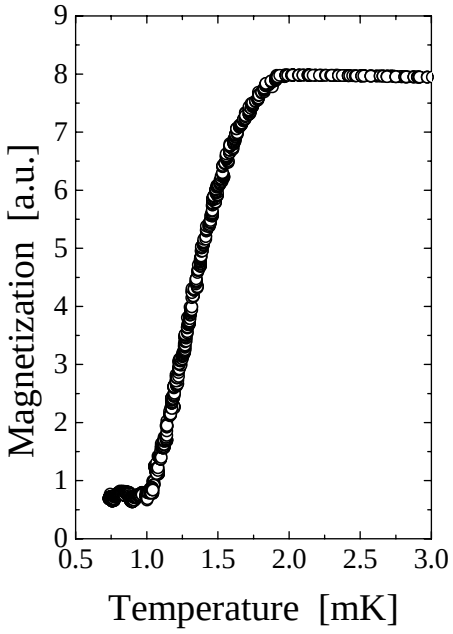

FIG. 2. Temperature dependence of the dc magnetization ("Meissner effect") of compacted Pt powder (packing fraction $f = 0.50$).

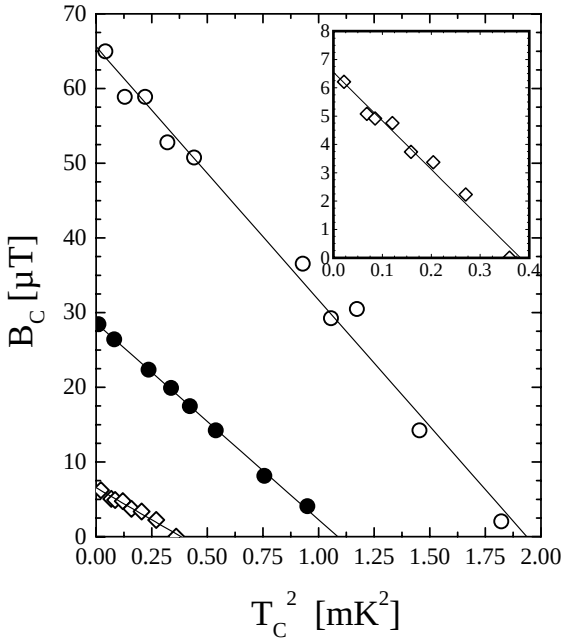

FIG. 3. Temperature dependences of the magnetic fields necessary to suppress superconductivity in Pt powder compressed at three different pressures: (∘) $f = 0.50$; (•) $f = 0.67$; (◇) $f = 0.80$. The inset shows an enlarged view of the data with $f = 0.80$. The solid lines are fits to the data using $B_C(T) = B_C(0)[1 - T^2/T_C^2]$.

application of small static magnetic fields leads to a decrease of these transition temperatures from their zero field values; the solid lines are fits of the function $B_C(T) = B_C(0)[1 - (T/T_C)^2]$ to the data. We obtain as zero temperature values for the critical fields necessary to suppress superconductivity $B_C(0) = 67$, 29, and 6.6 μT for $f = 0.50$, 0.67, and 0.80, respectively.

A fundamental aspect in a discussion of the results is the large surface to volume ratio of the compacted powder which could possibly lead to an appreciable lattice softening. This is considered to be an important mechanism responsible for the enhancement of the transition temperature, e.g., in granular nontransition superconductors [14]. Clearly, the effect of granularity, i.e., the dependence of the superconducting properties of platinum on different grain sizes and packing fractions, have to be studied systematically in the succeeding experiments. Equally important are further studies of the interplay between superconductivity and Stoner enhanced magnetism in platinum, as well as of the role of magnetic impurities on the superconductivity in the compacted powder, as, in the samples investigated so far, no formation of giant moments and the corresponding spin glass freezing was observed. These studies of the low temperature magnetic properties will be accompanied by magnetization measurements in the kelvin temperature range.

We conclude that the results of the measurements of ac susceptibility, dc magnetization (Meissner effect), and electrical resistivity are consistent with the observation of superconductivity in samples of compacted platinum powder. Based on the results of the thorough characterization of the powders, we may—to the best of our knowledge—rule out that our observations are caused by any impurity phase inside or on the surface of the samples. In this context, we mention that susceptibility measurements on compacted silver powder (grain size ≈ 0.1 μm, magnetic impurities about 2 ppm) do not show any indication of a superconducting transition down to a minimum temperature of about 0.1 mK. The discovery of superconductivity in compacted platinum powder should stimulate further experiments necessary to clarify the origin and the type of superconductivity in this new superconducting material.

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[8] K. Gloos, P. Smeibidl, C. Kennedy, A. Singsaas, P. Sekowski, R. M. Mueller, and F. Pobell, J. Low Temp. Phys. **73**, 101 (1988).

[9] We restrict ourselves in this publication to present results obtained with platinum powder Grade I of Alfa Johnson Matthey GmbH, Zeppelinstr. 7, D-76185 Karlsruhe, Germany. However, we have confirmed the results using another Pt powder from a different supplier (Goodfellow Metals Ltd., Cambridge Science Park, Cambridge CB4 4DJ, England, see also Ref. [10]).

[10] The microscopic analysis of the Pt powder of Alfa Johnson Matthey GmbH revealed a second maximum in the cluster size distribution at $\approx 0.5\ \mu$m; the amount of these smaller Pt clusters was estimated to less than 5%. The cluster size of the powder of Goodfellow Metals Ltd. appeared to be slightly larger than the Alfa powder ($\approx 3\ \mu$m) with only one maximum in the cluster size distribution.

[11] Results of dc arc emission spectroscopy (AES) were provided by a typical batch analysis of Alfa Johnson Matthey; inductively coupled plasma mass spectroscopy (PMS) was performed at FZ Rossendorf, Dresden, Germany. The only significant difference in both studies concerns the impurity content of V in the Pt samples: AES < 1 ppm, PMS ≈ 26 ppm. The reason for this discrepancy is unknown to us. The high purity of the investigated powder might possibly be related to the particular method the powder is produced by means of chemical processing.

[12] SQUID magnetometer S600, Cryogen. Consult. Ltd.

[13] AC Inductance and Resistance Bridge LR700, Linear Research Inc., San Diego.

[14] See, e.g., B. Abeles, Appl. Solid State Sci. **6**, 64 (1976); S. Matsuo, H. Sugiura, and S. Noguchi, J. Low Temp. Phys. **15**, 481 (1973).