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Brief Reports

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Knight shift in small platinum particles

J. J. van der Klink and J. Buttet
Institut de Physique Expérimentale, Ecole Polytechnique Fédérale de Lausanne,
CH-1015 Lausanne, Switzerland

M. Graetzel
Institut de Chimie-Physique, Ecole Polytechnique Fédérale de Lausanne,
CH-1015 Lausanne, Switzerland

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We have prepared small platinum particles on SiO_2 by a novel method, and observed the ^{195}Pt nuclear magnetic resonance. The signals are extremely broad, ranging essentially from a field-to-frequency ratio $H_0/\nu_0 = 1.14$ G/kHz (as in bulk Pt) to $H_0/\nu_0 = 1.10$ G/kHz (which is zero shift by convention). We suggest that the latter value is characteristic for Pt nuclei in a metallic environment at or near a clean surface.

INTRODUCTION

By magnetic resonance experiments on small metal particles one may either study intrinsic size effects,[1] such as those due to the discrete nature of the energy levels near the Fermi energy, or surface phenomena, due to the large ratio of the number of surface atoms to the number of volume atoms. In the case of platinum particles, surface effects appear to predominate: two groups have presented ^{195}Pt nuclear magnetic resonance results in recent years[2-6] that are qualitatively widely different, but both sets of data have been interpreted as surface phenomena. Yu, Gibson, Hunt, and Halperin[2] and Yu and Halperin[3] have performed experiments on unsupported samples prepared by an impregnation method on silica gel that was subsequently removed to increase the sample density. They find no change in resonance position, but a modest line broadening ΔH ($\Delta H/H$ less than 0.1%) that varies inversely with the average particle diameter. Slichter and co-workers[4-6] have reported results on alumina-supported samples. They find an extremely broad ($\Delta H/H$ several percent) resonance whose detailed features change with particle size. Most of their results reported so far were performed on samples with uncontrolled surface conditions, and they assign a prominent peak at low field (corresponding to a Knight shift $K \approx +0.9\%$) in the resonance spectrum to $Pt(OH)_6$ formed at contact of the surface with atmospheric air.

In this paper we present some results on silica-supported platinum particles, prepared by another method, and under controlled surface conditions. Our results are qualitatively similar to those the Slichter group obtained on a sample with a cleaned surface.

SAMPLE PREPARATION AND CHARACTERIZATION

We prepared an aqueous colloid of Pt particles by citrate reduction of H_2PtCl_6, according to a previously described technique.[7] A high-resolution electron microscopic study[8] showed that the particles so obtained are of diameter around 20 Å, and contain some ten atomic (111) planes of the bulk structure. As the next step we introduced SiO_2 (typical particle size 200 Å and surface density 200 m²/g) into the solution that then was dried by pumping at 20 °C under continuous stirring. For sufficiently large SiO_2/Pt ratio little coagulation of the deposited Pt particles occurred. The SiO_2-supported particles were subsequently treated in an all-glass apparatus by several cycles of oxidation by O_2 and reduction by H_2, alternated by abundant He flushing. We used a turbo-molecular pump and a cold trap to prevent contamination. If this treatment was performed at temperatures below

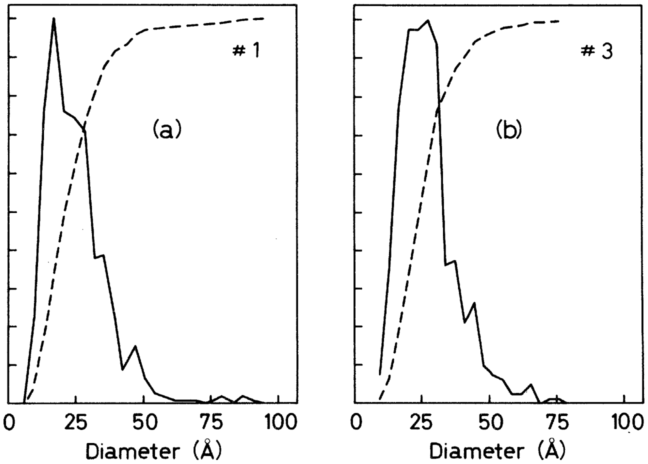

FIG. 1. Size distribution of Pt particles in two Pt/SiO_2 samples. Number of particles of given diameter counted vs diameter. (a) sample No. 1 and (b) sample No. 3. The dashed lines show the integrals of the distributions. Total number of particles counted is 631 for (a) and 533 for (b).

TABLE I. Most abundant trace elements in a SiO_2:Pt sample, in μg/gm, determined by neutron activation analysis.

Na	1.75×10^3
Mg	415
Al	890
Cl	1.52×10^3
Ti	843
Cu	30.2
Pt	4.27×10^4
K	188
Mo	14.1
Cr	14.9
Fe	33.5
Zn	155
Cs	11.9
Ni	< 480

400 °C, no significant increase in particle size was observed. After the last reduction, the samples were cooled down under a constant flux of He and sealed in glass ampoules. Their particle size distributions (see Fig. 1) were determined after the NMR data had been taken, by opening the ampoules and taking high-resolution electron micrographs of some of the sample. The Pt/Si ratio and the amount of a number of impurities were determined by neutron activation analysis (see Table I). In addition we checked for paramagnetic impurities by ESR, without detecting any. We report here on three samples so prepared: the one labeled No. 1 was treated at 400 °C and contained 4.6% by weight of Pt; sample No. 2 was prepared in the same way, but treated at 220 °C; sample No. 3 has been prepared with twice the amount of SiO_2. We therefore expect it to contain approximately 2.3% Pt. The oxido-reduction treatment of this sample was performed at 220 °C. The average-sized particles in these samples have a fraction of surface atoms of about one-half, but for those in the tail of the distribution this value drops an order of magnitude.

NMR RESULTS

The NMR equipment consisted of an Oxford 8T superconducting magnet, and a Bruker SXP pulsed NMR spectrometer with quadrature detection. A Datalab transient recorder interfaced to a Nicolet B-NC 12 computer permitted signal averaging and data treatment.

Generally speaking, two different methods can be used to extract spectral information from time-domain NMR signals; their applicability depends on the experimental circumstances. The first, and most widely used, method is based on the fact that, if the amplitude in Gauss of the exciting rf magnetic field H_1 is much larger than the spectral width ΔH to be studied, the time-domain free induction decay and the frequency-domain spectrum are each others Fourier transforms. The second method, mainly used in the opposite case $H_1 << \Delta H$ (where the Fourier transform of the free induction decay essentially represents the spectral characteristics of the exciting pulse), uses the fact that the integral over a spin echo is proportional to the amplitude of the spectrum at the measuring frequency ν_0. The full spectrum is then obtained by sweeping the static field H_0 (or eventually the frequency ν_0).

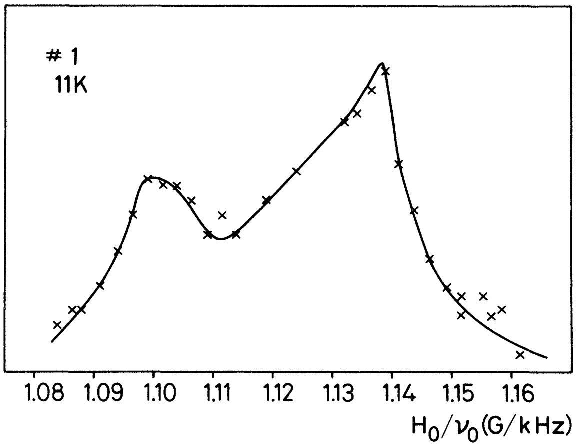

FIG. 2. ^{195}Pt NMR spectrum for sample No. 1. 4.6 wt. % Pt on SiO_2, measured by the field-swept spin-echo method. $T = 11$ K.

In Fig. 2 we show results for sample No. 1, obtained by the field-swept spin-echo method. The spectrum has $\Delta H/H$ of a few percent and extends from below the conventional zero-Knight shift position, $H_0/\nu_0 \approx 1.10$ G/kHz, to beyond the value observed in bulk platinum, $H_0/\nu_0 \approx 1.14$ G/kHz. These data have been obtained by a sequence of two pulses, with a 50-μsec interval between them. Since the spin-spin relaxation time T_2 and the attenuation due to the indirect spin-spin coupling[9] vary over the spectrum, they affect the measured amplitude differently at high and at low fields. At the present stage we have not corrected for this effect; from rough measurements, we estimate that corrections would increase the high-field end of the spectrum by about 25%. In Fig. 3 frequency-swept spin-echo data are shown for sample No. 3 as open circles, and the line drawn in Fig. 2 has been replotted for reference. The platinum content of No. 3 is near the limit of what is detectable (for such broad signals) in our spectrometer, and there is a considerable scatter in

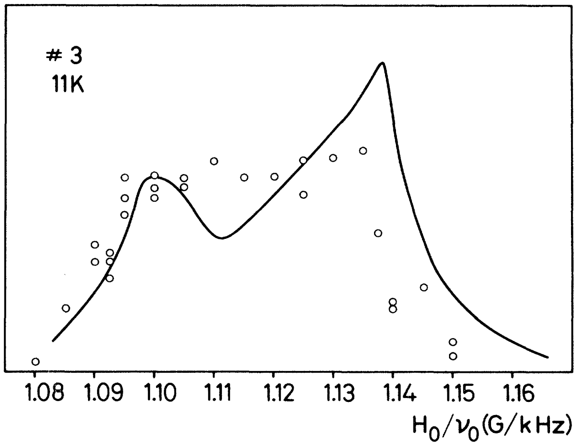

FIG. 3. ^{195}Pt NMR spectrum for sample No. 3, approximately 2.3 wt. % Pt on SiO_2 measured by the frequency-swept spin-echo method. The full line is the same as in Fig. 2. The decrease in intensity at the high-field end of the spectrum is attributed to a diminished number of large particles with respect to sample No. 1. $T = 11$ K.

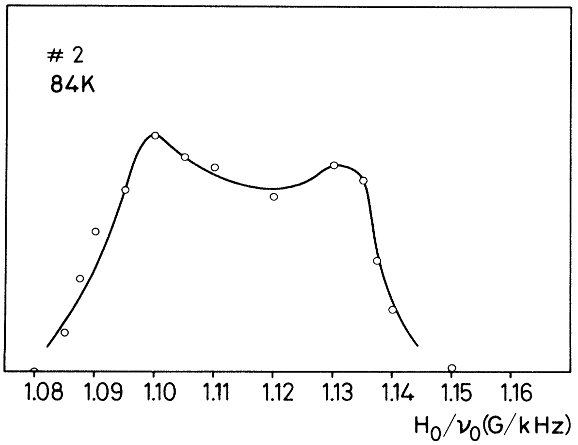

FIG. 4. ^{195}Pt NMR spectrum for sample No. 2 measured by the frequency-swept spin-echo method. Sample preparation as that of sample No. 3, but with a higher Pt/Si ratio. $T = 84$ K.

the data. Still it seems fair to conclude that the low-field end of the spectrum occurs at the same position as in sample No. 1, but that the high-field end has shifted to slightly lower values. The total width $\Delta H/H$ is again of the order of a few percent. Similar spectra have been obtained at higher temperatures: as an example we show in Fig. 4 the frequency-swept spectrum at 84 K of sample No. 2.

At all fields and for the three samples the echo amplitude was independent of the pulse repetition rate in the range 70–5 Hz, showing that the spin-lattice relaxation time T_1 is shorter than ≈ 10 msec. Rough measurements of T_2 at $T = 11$ K indicate values varying from 700 μsec at zero Knight shift to 400 μsec at the bulk position.

DISCUSSION

The qualitative agreement between our results and those of the Urbana group is very clear [cf. especially Fig. 8(b) of Ref. 4]. Plotted on the scale of our figures, the resonance line observed by Yu and Halperin[3] on a sample with average diameter 33 Å has a width approximately equal to the thickness of the drawn lines and occurs at the bulk Knight shift. The only significant difference between the preparation methods used at Urbana[4] and at Northwestern[3] is that the latter group washed away the support; their NMR results however, are very different. On the other hand, the methods of sample preparation used by the Urbana group and by us are very different, but give similar NMR results.

The upper limit for T_1 ($T_1 < 10$ msec) that we observe at $H_0/\nu_0 = 1.10$ G/kHz indicates that this signal is due to ^{195}Pt nuclei in a metallic environment. (The *total* Knight shift may well be zero without T_1 becoming very long. The assumption in Fig. 2 of Ref. 5 is only valid for simple metals, not for Pt). The observed values for T_2 indicate that the homogeneous linewidths are of the order of a few kHz everywhere in the spectrum, which has a total width of more than 3 MHz. The total spectrum therefore is a nonresolved superposition of a large number of different lines, due to distinct sites in the platinum particles.

It is instructive to compare this situation with what is observed in Pt alloys. In dilute alloys separate signals are found for the nearest[10] and very often for the next-nearest[11] neighbors of an impurity. In more concentrated alloys, the position of the "bulk" resonance is shifted from its value in pure Pt towards that of the impurity neighbor, the latter being unmodified.[10] Making an analogy between the surface sites in a small particle and the nearest neighbors to the defect in an alloy, between the subsurface layer and the next-nearest neighbors and so on, we expect all resonances to lie inside the interval between the nearest-neighbor (the surface) resonance and the bulk resonance. In addition, if the surface/volume ratio is high the position of the "bulk" resonance should shift towards that of the surface, the latter being unmodified. This reasoning leads to the identification of the signal at $K = 0$ (at 1.10 G/kHz) with the surface resonance, and from the T_1 estimate we know that it is due to nuclei in a metallic environment, rather than tied in chemical bonds. It also shows that in samples that contain *only* small particles (and no accidental bigger ones) the observed "bulk" peak may shift to lower fields when the particle size decreases.

Actually, many distinct sites will exist in the surface layer as well as below. If the particles are cubo-octahedra, there will be surface sites in (100) and (111) planes and on (or near) edges between them. The fractions of each of those sites are rapidly varying functions of particle size.

The details of the NMR spectrum will therefore vary with the particle size distribution. For example, the signal intensity at the bulk position due to one particle of 100 Å diameter is comparable to that from a thousand particles of 20 Å.

Such a frequency distribution is hard to verify from the analysis of electron micrographs, but might have occurred in sample No. 1 due to the higher temperature at which the oxido-reduction cycle was performed. A considerable reduction in signal intensity at the bulk position (as in sample No. 3) has also been observed by Slichter *et al.* for samples with mean diameters below 30 Å.

Very recently, Weinert and Freeman[12] have calculated the (spin-only) Knight shift of a five-layer Pt (001) film, and obtained that the surface layer should have a more positive Knight shift ($K = -0.6\%$) than the central layer ($K = -4.1\%$). The latter value is in excellent agreement with the bulk spin-only value of $K = -4.08$ that Shaham, El-Harany, and Zamir[13] deduced from experiment and in good agreement with earlier data by Clogston, Jaccarino, and Yafet.[14] (The total Knight shift contains an additional positive orbital contribution.)

The present results on Pt particles deposited on silica lend strong support to Weinert and Freeman's interpretation[12] of earlier data[14] on Pt catalysts, prepared on alumina by an impregnation method: the value of the Knight shift at a clean Pt surface is near zero.

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