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Observation of Conduction-Electron Density Oscillations at the Surface of Platinum Particles

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Anomalously large ^{195}Pt NMR linewidths have been observed in platinum particles with diameters ranging from 33 Å to 200 Å. Spin-echo measurements revealed the presence of nuclear spin-exchange diffusion in large magnetic field gradients attributable to the large indirect exchange interaction in platinum. These data indicate that there are electron spin-density oscillations near the platinum surface consistent with a simple model ascribing free-electron behavior to the *s*-like conduction electrons.

There has been considerable theoretical and experimental interest in the surface electronic properties of the transition metals. In this work we have applied NMR techniques to the study of platinum metal clusters which broach the size regime of interest to heterogeneous catalysis where the fraction of atoms at the surface approaches unity. In such particles the discrete nature of the conduction-electron level spectrum becomes important giving rise to quantum effects[1] that scale inversely with the particle volume. Significantly, in our work, we see no evidence of this phenomenon in particles of diameter as small as 33 Å and at temperatures near 1.7 K. Another important effect is the direct influence of the metal surface on the electron density. We have discovered that ^{195}Pt NMR is very sensitive to this.

The samples were made from a silica-gel-supported platinum catalyst fabricated by a well-established impregnation technique.[2] The particles were spheroidal and essentially strain and defect free.[3] The silica gel support was removed and 0.3 g of the remaining platinum powder was loaded into a quartz sample chamber and sealed in a helium atmosphere. After NMR experiments were performed the sample was heated *in situ* for five hours to increase the particle size systematically prior to the next sequence of experiments. For size characterization, electron microscopy, nitrogen adsorbtion (Brunauer-Emmett-Telks method), and hydrogen chemisorption (titration method)[4] measurements were performed (Table I).

Pure platinum and its alloys have been investigated extensively[5] by NMR. Some of the relevant

TABLE I. The characterization of the various samples studied including the heat treatment temperature and particle diameters obtained by electron microscope (EM) studies, and surface areas and diameters obtained by N_2 adsorption [Brunauer-Emmett-Teller (BET)] and by titration of H_2 on the Pt surface (H_2). The surface area measurements of *d* have an estimated accuracy of 10%. The first two samples were not heated. Samples 3, 4, and 5 were obtained by heating sample 2.

No.	*T* (°C)	EM *d* (Å)	BET (m^2/g)	BET *d* (Å)	H_2 *d* (Å)
1		33 ± 11	...	...	36
2		50 ± 10	49	57	62
3	450	100 ± 20	20	140	132
4	550	140 ± 20	17	170	160
5	650	200 ± 40	13	218	258

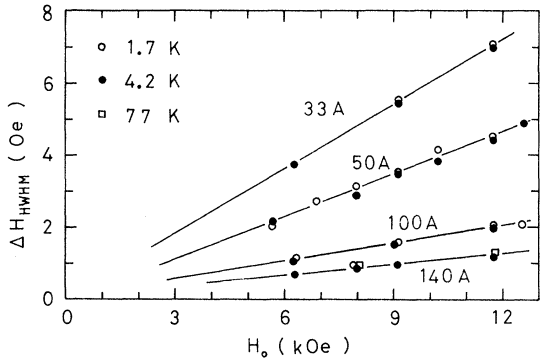

FIG. 1. Half width at half maximum linewidth measurements as a function of magnetic field for various temperatures and particle sizes.

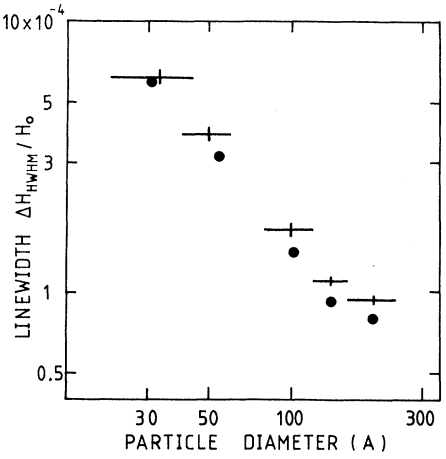

FIG. 2. The normalized linewidths as a function of particle diameter determined by electron microscopy and compared with a simple no-parameter model.

properties are that ^{195}Pt is 34% abundant, and has spin $\frac{1}{2}$. It is free of quadrupole effects and an indirect Ruderman-Kittel exchange coupling gives narrowing of the dipolar linewidth. This contribution to the spin Hamiltonian is written as $H_{ex}=\frac{1}{2}J\sum_{ij}\vec{S}_i\cdot\vec{S}_j$ where the sum is over near-neighbor nuclear spins and $J/h=(4.0\pm0.2)\times10^3$ Hz as determined from alloy studies.[5] It dominates the other spin interactions by an order of magnitude, i.e., dipolar and pseudodipolar terms.

In our work we used a coherent, heterodyne, pulsed NMR spectrometer interfaced to a minicomputer for fast-quadrature Fourier-transform spectroscopy. At 10 MHz, signal averaging of the data could begin 5 μsec after a 4-μsec 90° pulse. Experiments were performed between 5 and 13 kOe and from 1.7 to 4.2 K although some linewidth measurements were taken at 77 K. All small-particle Knight shifts were found to be $(-3.4\pm0.05)\%$ in precise agreement with that of bulk material.[6] Similarly, no size effects were found in the Korringa constant $T_1T=29\pm1$ msec·K again in excellent accord with published values.[6] However, the NMR linewidth was found to be temperature independent and to increase dramatically, proportional to the magnetic field and approximately inversely with particle diameter d, as shown in Figs. 1 and 2. This effect is much larger than demagnetization broadening[7] and is unaffected by *external* surface conditions which were varied through chemisorption of oxygen or hydrogen. Since the surface-to-volume ratio scales as d^{-1} these results suggest that there is a Knight-shift distribution related to the particle surface.

That the NMR line is inhomogeneously broad-

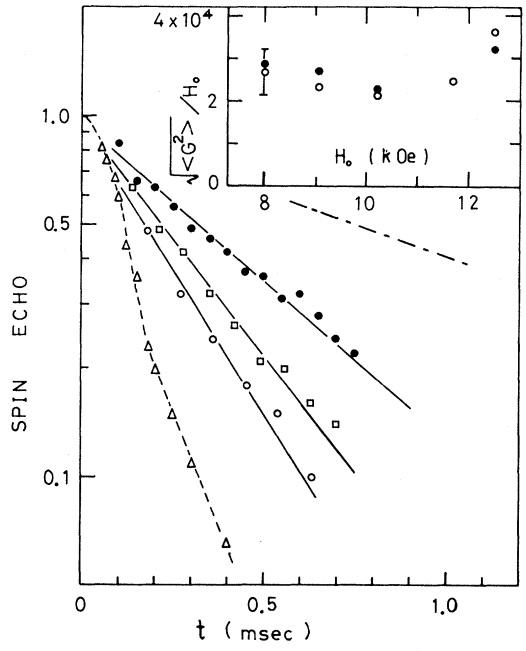

FIG. 3. Spin dephasing measurements for sample 2 at 8 MHz and 4.2 K for the spin-echo technique, triangles and dashed line, and the modified Carr-Purcell method, solid lines. For the latter, solid circles, squares, and open circles correspond to values of $2\tau=50$, 70, and 90 μsec, for which the slopes of the echo amplitudes versus time, including data omitted from the figure for reasons of clarity, are (1.92, 2.38, 2.94, 3.33, 3.70, 3.85, and 4.00)$\times10^3$ sec^{-1} for values of 2τ of 50, 60, 70, 80, 90, 100, and 150 μsec, respectively. The inset shows the rms field gradient deduced at a number of applied fields.

ened was demonstrated by our observation of a spin echo after a (90°,180°) pulse sequence. However, it was found that the spin-echo envelope, as shown in Fig. 3 by a dashed line, first decayed very rapidly and nonexponentially in time, and later exponentially, in contrast to that for 5-μm-diam particles of Pt (bulk) which exhibit exponential behavior such as that shown by the dash-dotted curve in Fig. 3. We found that the logarithm of the spin-echo amplitude varied as t^3 for $t<100$ μsec suggesting[8] that diffusion was observed. We confirmed that indeed spin diffusion was operative by performing experiments with two "self-correcting" modifications[9] of the Carr-Purcell pulse method: $(90_x^0,\tau,180_y^0,2\tau,180_y^0,\ldots)$; $(90_x^0,\tau,180_x^0,2\tau,180_{-x}^0,\ldots)$. Carr and Purcell[10] showed that the effects on the echo amplitude of diffusion in a constant magnetic field gradient G could be reduced significantly by applying a series of 180° pulses. Then the amplitude $F(t)$ of the spin echo between pulses is given by

$$\ln F(t) = -(D\gamma^2G^2\tau^2/3 + T_2^{-1})t,$$

where D is the spin diffusion constant, γ the gyromagnetic ratio, and T_2 the nondiffusive spin-spin relaxation time. For a nonuniform field gradient this expression can be applied, replacing G^2 by $\langle G^2\rangle$, provided $\tau^2 t < 3/\gamma^2\langle G^2\rangle D$. [For sample 2, $(12/\gamma^2\langle G^2\rangle D)^{1/3} \simeq 100$ μsec.] Our data clearly exhibit this behavior for t and $2\tau < 100$ μ sec. For larger values of 2τ, $F(t)$ becomes independent of τ, consistent with the (90°,180°) pulse results for large pulse separations. This may be evidence for boundary-limited diffusion.[11] The frequency and particle-size dependence of this phenomenon is discussed in this context elsewhere.[12] Extrapolation of the diffusion measurements to zero τ gives a value of $T_2 = 1.2 \pm 0.2$ msec in excellent agreement with the *strain-free* bulk platinum value.[6,13] Experiments were performed in magnetic fields H_0 from 8 to 12 kOe from which $D\langle G\rangle^2/H_0^2$ was obtained. We have calculated the spin diffusion constant for the longitudinal component of the magnetization of platinum, $D_z = 4.0 \times 10^{-12}$ cm^{2}sec^{-1}, using Redfield and Yu's moment method.[14] These authors point out that there is no distinction between the diffusion constants for transverse and longitudinal components of the magnetization in the case of the rotationally invariant indirect exchange interaction, and that this result can be reasonably applied even in the presence of an inhomogeneous magnetic field, provided the inhomogeneity from site to site is less than the local field. On this basis we proceed to use D_z to interpret our measurements of the decay of the transverse components of the magnetization and find the average field gradient (inset to Fig. 3) for sample 2 to be $\langle G^2\rangle^{1/2}/H_0 = (2.7 \pm 0.5) \times 10^4$ cm^{-1}. Although the difference in the static magnetic field between near neighbors in our experiments becomes comparable with the homogeneous local field, 5.6 Oe, it is apparently not sufficiently large to produce localization of the spin magnetization currents.[15]

We have attempted to model the observed Knight-shift distributions by considering the perturbation introduced by the metal surface on the conduction electrons. In this treatment we have only allowed changes in the s-electron contribution to the Knight shift as a response to the presence of the surface, and the s electrons were taken to be free fermions confined to a sphere. The spatial variations of electron charge and spin density were then calculated for each particle size up to 200 Å. The electron density $\rho_e(r)$ was obtained by summing all partial-wave contributions of wave vector k up to the Fermi wave vector k_F. Similarly, the electron spin density $n_s(r)$ was obtained by restricting[16] this sum to be near k_F. The results in Fig. 4 are for the case of a spherical particle of radius $R = 27$ Å. Evidently there are Friedel oscillations of period $\pi/k_F = 0.8$ lattice constant which die out within three lattice spacings of the surface. $\rho_e(r)$ and $n_s(r)$ are similar but phase shifted by about $\pi/2$.

The NMR line was generated by summing the elemental contribution from every ^{195}Pt nucleus in the particle. The Knight shift of each element

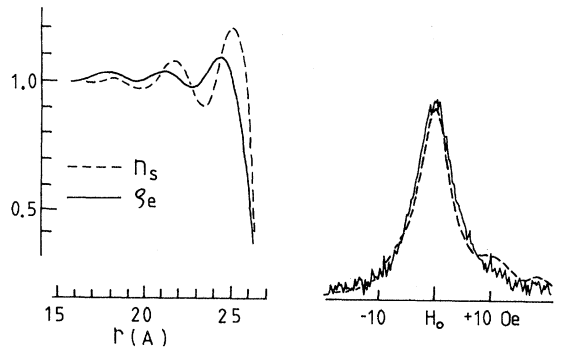

FIG. 4. The calculated free-electron charge (ρ_e) and spin (n_s) densities for a 27-Å-radius particle. The corresponding NMR line is shown as a dashed curve compared with the measured result for sample 2 at 10 kOe and 4.2 K.

was taken to be $K(r)=K_{\text{bulk}}+\Delta K_s(r)$, where

$$\Delta K_s(r)=[n_s(r)/n_{s,\text{bulk}}-1]K_{s,\text{bulk}}$$

and $K_{s,\text{bulk}}=+1.0\%$.[17] The elemental linewidth was determined by our spin-echo measurements of the homogeneous broadening. A direct comparison of the observed transformed spectrum and the computed one is shown in Fig. 4. The computed linewidths for different particle sizes are given in Fig. 2. The agreement between the experiment and the naive no-parameter model is very good even though no exchange or correlation effects have been included.

Using the same model for $R=27$ Å we calculated the average square field gradient between near-neighbor nuclei normalized to the external field, finding $\langle G^2\rangle^{1/2}/H_0=3.5\times10^4$ cm^{-1} in qualitative agreement with the experimental result of $(2.7\pm0.5)\times10^4$ cm^{-1} for sample 2. The calculated linewidths vary as $\sim d^{1.2}$ in agreement with experiment as compared with the work of Charles and Harrison[18] who predicted a $d^{-1/2}$ dependence.

It remains to be seen how more sophisticated self-consistent models including d-electron behavior will compare with these experimentally observed parameters. However, we can infer that the anomalous line broadening observed in platinum particles is attributable to electron spin-density oscillations near the metal surface, a phenomenon which may accout for reports of NMR line broadening observed in lead and tin small metal particles.[18,19]

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