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NMR evidence of a spatially resolved oscillation in the $E_{\rm f}$ -LDOS in a nanoscale platinum electrocatalyst

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Abstract

Indirect nuclear spin–spin *J*-coupling measurements have been carried out on a conducting, carbon-supported 8.8 nm platinum electrocatalyst by using ¹⁹⁵Pt NMR. The *J*-coupling values show a marked variation across the spectrum. These *J*-coupling values were then transformed into the corresponding s-like Fermi level local density of states $D_s(E_f, x)$, where x is the distance from the particle surface, revealing a spatially resolved oscillatory decay in $D_s(E_f)$ which is responsible for the line broadening of the bulk peak in the ¹⁹⁵Pt NMR spectrum. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

There is currently considerable interest in understanding the detailed electronic properties of high-surface-area (transition) metal nanoparticle catalysts. These materials provide an ideal framework in which it is possible to investigate the diverse behaviors of electrons confined within a nanoscale, three-dimensional space, together with the influence of the metal surface on bulk electronic properties. Nuclear magnetic resonance (NMR) experiments have proven to be of considerable value in learning more about the electronic properties of such metal nanoparticles [1,2]. The

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peak position and width of the NMR spectra of nanoparticles reflect the Fermi level local density of states ($E_{\rm f}$ -LDOS) and its spatial distribution. Spin-lattice relaxation (T_1) measurements provide added insight into the dynamic coupling between the nuclear spin system and the low lying electronic excitations, while spin-spin relaxation (T_2) measurements serve as an effective means to estimate the strengths of the various couplings between different nuclear spins. Unusually broad NMR spectra have been obtained for dilute alloys [3], as well as for small metal particles of Pb [4], Ag [5] and Pt [6] and Bardeen–Friedel [7,8] oscillations have been invoked to account for such broad NMR lines. However, no direct observation of a spatially varying oscillatory behavior of the $E_{\rm f}$ -LDOS, due to the presence of the metal surface, has yet been reported.

¹⁹⁵Pt NMR of nanoscale Pt particles [9] can, in principle, permit such a detailed study of the

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spatial variation of the $E_{\rm f}$ -LDOS across a given particle. This is possible because the ¹⁹⁵Pt NMR spectra are extremely broad, covering almost a 2.5 MHz range (at 8.5 T), and nuclei in individual platinum layers resonate at different frequencies, due to significant changes in local electronic properties caused by the presence of the particle's surface. The exponential healing model [1,10] relates the Knight shift of atoms at a given radial position to their distance from the surface, and such a spatial dependence provides the conditions necessary for observation of the indirect nuclear spin–spin *J*-coupling [11,12] between neighboring Pt atoms [13] as a function of radial position.

Here, we report the ¹⁹⁵Pt NMR spectrum of Pt nanoparticles having an average particle size of 8.8 nm together with corresponding *J*-coupling measurements. We observe an across-the-spectrum (from 1.1000 to 1.1388 G/kHz) variation in the *J*-coupling between neighboring ¹⁹⁵Pt nuclear spins. Using the exponential healing model [1,10], we obtain evidence for a spatially varying *s*-like $E_{\rm f}$ -LDOS arising due to the presence of the particle's surface. This spatial variation of $D_{\rm s}(E_{\rm f})$ can be expected to contribute to the intrinsic width of the 'bulk' NMR peak observed in small Pt particles.

2. Theoretical considerations

In order to deduce the relationship between $D_{\rm s}(E_{\rm f})$ and radial position, we use the method developed by Slichter et al. [13] to derive *J*-couplings from the spin echo envelope obtained as a function of τ , using a Hahn echo sequence $(\pi/2-\tau-\pi)$

$$S(\tau) = S_0 \exp(-2\tau/T_2) \{ B_0 + \exp(-(\tau/T_{2j})^2) \\ \times [B_1 \cos(J\tau) + B_2 \cos(2J\tau)] \}.$$
(1)

Here, T_2 is the intrinsic spin–spin relaxation time, T_{2j} accounts for the effects due to a slight spread in J among different spin pairs, and B_m are the Fourier coefficients satisfying $\sum B_m = 1$. J is determined at a series of spectral positions (Knight shifts). The distance from the particle surface can be obtained by employing the exponential healing model [10]

$$x = x_0 \ln[(K_{\text{surf}} - K_{\text{bulk}})/(K(x) - K_{\text{bulk}})], \qquad (2)$$

where K_{bulk} and K_{surf} are the Knight shifts of bulk and of surface Pt atoms, respectively, and x_0 is the characteristic healing length (see [1,10] for detailed discussion of the exponential healing model). In a metal, the conduction electron mediated *J*-coupling is almost entirely determined by the s-like E_{f} -LDOS [1,14,15] and it is proportional to $K_{\text{s}}(x)$, the Knight shift caused by s-like electrons. Assuming that local variations in $K_{\text{s}}(x)$ arise solely from variations in the s-like E_{f} -LDOS, one can readily deduce the following relationship [16] between the s-like E_{f} -LDOS, $D_{\text{s}}(E_{\text{f}}, x)$, and the local *J*-coupling, J(x), measured by ¹⁹⁵Pt NMR:

$$D_{\rm s}(E_{\rm f},x) = [0.098 + 0.62/J(x)]^{-1}.$$
 (3)

This enables a direct measurement of $D_s(E_f, x)$. It might also, in principle, be possible to deduce $D_s(E_f, x)$ from a two-band model analysis of T_1T information, however, van der Klink and coworkers [17] have previously shown that there are large uncertainties associated with such D_s determinations, due to the highly non-linear relationships between T_1T, K and D_s, D_d . Consequently, *J*-coupling measurements appear to be the method of choice for investigating the spatial variation of $D_s(E_f, x)$ which arise due to the presence of metal surface. Eqs. (1)–(3) are used in analyzing the experimental data described in the following section.

3. Experimental

Commercially available, carbon-supported Pt nanoparticles were obtained from E-TeK. Transmission electron microscopy (TEM) results indicated that this catalyst had a very narrow particle size distribution (8.8 ± 0.6 nm). The surfaces of the as-received particles were electrochemically cleaned (at room temperature) and the particles were then transferred into an NMR tube. Details of the NMR measurements were reported previously [16]. The spectrum was recorded point-bypoint by manually varying the carrier frequency between 74 and 78 MHz in steps of 100 kHz. T_1 was determined by using a saturation-comb spinecho method. The *J*-couplings were obtained by fitting the spin-echo envelope, measured by using the $\pi/2-\tau-\pi$ Hahn echo sequence as a function of τ , to Eq. (1). In three cases, *J*-couplings were determined at two radio frequency field strengths in order to provide an estimate of the accuracy of the *J* values so obtained, as discussed below.

4. Results and discussion

We show in Fig. 1a the ¹⁹⁵Pt NMR spectrum of the 8.8 nm platinum catalyst sample and in Fig. 1b we show T_1 relaxation curves, measured at three different spectral positions, at 80 K. Different symbols represent data measured at different times, demonstrating good reproducibility. The spectrum is very similar to that of sample Pt-15-R in [18], which has a similar average particle size, except that our sample has no Pt oxide peak at 1.089 G/kHz. The solid lines in Fig. 1b are the single exponential fits to the data, indicating that a single 'class' of Pt atoms resonate at a given frequency [14,15]. The T_1 values obtained are 712, 635, and 331 µs at 1.1000, 1.1058, and 1.1375 G/kHz, respectively. The T_1 value at 1.1375 G/kHz (the high-field peak position), yields a $T_1T = 0.027$ s.K, which is in good agreement with the tabulated value for bulk platinum [3], indicating a bulk-like environment for these atoms. The decreases in T_1 when moving towards highfield are also in agreement with observations in gas phase, oxide-supported small Pt particles [17,18] and are mainly due to changes in the d-like $E_{\rm f}$ -LDOS [19]. The consistency between the data reported here and those found for oxide-supported Pt particles regarding the lineshape, T_1 and T_2 , clearly indicates the same underlying physics in both systems.

In Fig. 2a, we show representative spin-echo envelopes, recorded at different spectral positions. The solid lines are fits to Eq. (1). The values of the fitting parameters for all 11 spin-echo envelopes are given in Table 1. The surface atoms resonate at 1.1000 G/kHz while atoms at the center of a nanoparticle (where a bulk-like environment exists) give rise to resonances in the vicinity of 1.138 G/kHz (the ¹⁹⁵Pt NMR frequency of bulk platinum). According to the exponential healing model, as one moves from the surface to the interior of a



Fig. 1. (a) Point-by-point ¹⁹⁵Pt NMR spectrum of an 8.8 nm, carbon-supported clean surface Pt electrocatalyst. (b) T_1 relaxation curves measured at 80 K and the corresponding single exponential fits (solid lines). Different symbols represent data measured at different times, demonstrating excellent reproducibility.

nanoparticle, the average Knight shift of Pt atoms in a given layer varies exponentially with the distance from the surface. Therefore, for atoms near the centers of the nanoparticles, the gradient in Knight shift is expected to be very small. For data at 1.1375 and 1.1380 G/kHz, a B_3 term was needed in Eq. (1) in order to obtain the best fits, most probably due to the smaller gradient of the Knight shift expected at these positions. Of course, in some cases, the oscillations are less pronounced



Fig. 2. (a) Spin-echo envelopes at different spectral positions, measured at 80 K. Sample as in Fig. 1. Representative error bars are shown on the spin-echo envelope at 1.138 G/kHz. The solid lines are the fits to Eq. (1) and all the fitting parameters obtained are shown in Table 1. The curve measured at 1.1204 G/kHz (open circles) has a reduced $\omega_1/2\pi$ (42 versus 62.5 kHz). (b) Spin-echo envelopes measured at 1.100 G/kHz together with fitted lines (Eq. (1)). (\bullet) $\omega_1/2\pi = 62.5$ kHz; (\Box) $\omega_1/2\pi =$ 42 kHz. The J values deduced are 6.9 (\bullet) and 6.5 (\Box) kHz.

than in other cases, which could compromise the accuracy of the *J*-couplings determined. To assess this possibility, we therefore determined *J* values at two radio frequency field strengths, at 1.1000 (the surface position), 1.1204 and 1.1324 G/kHz. Fig. 2b shows results at 1.1000 G/kHz. While the T_2 and B_i fitting parameters vary with r.f. field strength (since fewer neighboring Pt atoms are excited and thus contribute to *J* modulation at the reduced r.f. levels), the *J*-values are remarkably consistent: 6.9 (6.5) kHz at 1.100 G/kHz; 3.0 (3.0)

kHz at 1.1204 G/Hz and 4.1 (3.8) kHz at 1.1324 G/ Hz (Table 1), giving good confidence in the J couplings determined. These were then used to obtain the $D_s(E_f)$ values shown in Table 1.

Inspection of the $D_s(E_f)$ results shown in Table 1 indicates that there is a clear oscillation in $D_s(E_f)$ across the spectrum. This result is of interest since it represents the first experimental observation of a spatially resolved oscillatory variation in $D_s(E_f)$ caused by the presence of a metal surface. Moreover, the experimental results can be fit to a simple relationship which has the essence of a Bardeen–Friedel oscillation [20]:

$$D_{\rm s}(E_{\rm f}, x) = D_{\rm s}(E_{\rm f}, \infty) + b\sin(2k_{\rm F}x)/2k_{\rm F}x.$$
 (4)

The solid line in Fig. 3 represents the fit to Eq. (4) which gives the following results: $D_{\rm s}(E_{\rm f},\infty) =$ 3.5 atom⁻¹ · Ry⁻¹, $k_{\rm F} = 6$ nm⁻¹, and b = 1.5atom⁻¹ · Ry⁻¹. Notice that $\sin(2k_F x)/2k_F x$ is an asymptotic form of oscillation but for simplicity, it is used here to approximate the behavior over the whole range. The value of $D_s(E_f, \infty)$, 3.5 atom⁻¹. Ry^{-1} , is also very close to the accepted value for bulk Pt [17], 4 atom⁻¹ · Ry⁻¹. Assuming each Pt atom contributes one s-like electron, the s-like electron density for bulk Pt would be $6.1 \times$ 10^{22} cm⁻³. By following the simplest model for free electrons [21], one obtains $k_{\rm F} = 12 \text{ nm}^{-1}$, about twice as large as the value we find. In other words, the value of 6 nm⁻¹ for $k_{\rm F}$ indicates a much longer decay length than that would be expected from the jellium model. The oscillatory variation in $D_{\rm s}(E_{\rm f})$ beyond 0.4 nm (Fig. 3) also indicates that the influence of the metal surface goes at least three layers inside the particles, in contrast to the predictions based on the jellium model. This conclusion is consistent with other results obtained on Ag particles [5] and in metallic spin-glasses [22], and suggests that much of the observed broadening of the bulk-like peak in ¹⁹⁵Pt NMR spectra of such systems [23] can be attributed to the spatial variation of the $D_{\rm s}(E_{\rm f})$. In summary, these results represent the first experimental observation of a spatially resolved oscillatory variation of the $D_{\rm s}(E_{\rm f})$ caused by the presence of a metal surface, which appears to be responsible for the intrinsic broadening of the Pt NMR bulk peak in ¹⁹⁵Pt NMR spectra of nanoparticle systems.

H/v	J	T_2	T_{2J}	B_0	B_1	$B_2^{\rm a}$	$D_{\rm s}(E_{\rm f})$
(G/kHz)	(kHz)	(µs)	(μs)				$(\operatorname{atom} \cdot \mathbf{Ry})^{-1}$
1.1000	60101	10.5		0.02	0.07	0.01	5.2 () 0.2 () 0.1)
1.1000	6.9 ± 0.4	186	441	0.92	0.07	0.01	5.3 (+0.2/-0.1)
	(6.5 ± 1.7)	(209)	(∞)	(0.97)	(0.03)	(0.0)	5.2 (+0.6/-0.8)
1.1058	4.8 ± 0.3	171	283	0.79	0.14	0.07	4.4 ± 0.2
1.1145	3.5 ± 0.3	168	299	0.69	0.31	0.0	3.6 ± 0.2
1.1204 ^b	3.0 ± 0.3	175	213	0.52	0.43	0.06	3.3 ± 0.2
	(3.0 ± 0.4)	(165)	(294)	(0.77)	(0.23)	(0.0)	3.3 ± 0.3
1.1249	2.6 ± 0.2	181	436	0.45	0.38	0.17	3.0 (+0.1/-0.2)
1.1294	3.6 ± 0.2	124	293	0.49	0.41	0.10	3.7 ± 0.1
1.1324 ^b	4.1 ± 0.2	119	459	0.51	0.39	0.10	4.0 ± 0.1
	(3.8 ± 0.4)	(123)	(825)	(0.71)	(0.29)	(0.0)	3.8 (+0.3/-0.2)
1.1375	4.2 ± 0.2	91	695	0.43	0.39	0.14 ^c	4.1 ± 0.1
1.1380	3.8 ± 0.2	107	403	0.42	0.39	0.14 ^c	3.8 ± 0.1
1.1388	3.2 ± 0.3	128	290	0.49	0.41	0.10	3.4 ± 0.2

Fitting parameters to Eq. (1) for spin-echo envelopes and $D_s(E_f)$ values

^a B_2 's were obtained from $B_2 = 1 - B_0 - B_1$.

Table 1

^b The values in parentheses are the fitting parameters obtained from the experimental data taken with an irradiation field $\omega_1/2\pi = 42$ kHz, smaller than the $\omega_1/2\pi = 62.5$ kHz value used for all other data. See text for discussion.

^c These B_2 's were fitting parameters and $B_3 = 1 - B_0 - B_1 - B_2$.



Fig. 3. The s-like $E_{\rm f}$ -LDOS as a function of distance from the particle surface, showing oscillatory behavior. The error bars were estimated by using Eq. (3) under the assumption that the uncertainty in s-like $E_{\rm f}$ -LDOS arises solely from the uncertainty in J(x) which was given directly by the five-parameter fit. The solid line is the fit to Eq. (4) (see the text for discussion). The open squares are from data measured at a reduced r.f. field strength.

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