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NMR of platinum catalysts. III. Microscopic variation of the Knight shifts

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The authors report observation of slow beats in the envelope of spin-echo decays in the ^{195}Pt NMR of small particles Pt supported on alumina. The beats are shown to arise from the interplay between the Knight-shift inhomogeneity present in the small particles and the pseudoexchange coupling J between neighboring nuclear spins. $J/2\pi$ is found to be 4.2 kHz.

I. INTRODUCTION

In small platinum particles, ^{195}Pt nuclei exhibit NMR properties vastly different from those in bulk pure Pt metal. This fact has been illustrated numerous times in the preceding two papers (Refs. 1 and 2, hereafter called papers I and II). In this paper, we discuss a phenomenon which is yet another manifestation of this fact, the existence of so-called "slow beats" (see also Refs. 3 and 4).

We collect data by the method of spin echoes in which two rf pulses separated by a time τ_d cause an NMR signal, the so-called spin echo, to form a time τ_d after the second rf pulse. Under many circumstances, the echo amplitude decays exponentially with the time $2\tau_d$ between the first pulse and the echo. Under special circumstances, there is an oscillation superimposed on this decay. This oscillation is called the slow beat.

The slow beat (and the corresponding steady-state frequency splittings) was first discovered in the NMR spectra of molecular liquids[5,6] and was shown to arise from the interplay of chemical shifts and spin-spin couplings. In fact, it was these phenomena which led to the discovery of the so-called nuclear pseudoexchange coupling in molecules, a coupling which persists despite the molecular tumbling.

In pure bulk ^{195}Pt, the nuclei are coupled to their neighbors through the dipolar, pseudodipolar, and pseudoexchange interactions. The latter coupling dominates, but there is no slow beat since all nuclei experience the same chemical and Knight shifts.

In small Pt particles, however, the NMR absorption line is inhomogeneously broadened by the Knight shift interaction. As we explain, it is this broadening which makes it possible to observe the slow beats in our sample of small Pt particles. In fact, we observe slow beats even for the nuclear spins which are in the deep interior of the largest particles in our sample—100 Å in diameter or more. We conclude from our data that even in Pt particles as large as these, the electronic environment is distinctly different from that of bulk Pt metal.

In Sec. II we review the basic description of the slow beat phenomenon, generating equations to deal with the case of small Pt particles. We describe the samples in Sec. III. In Sec. IV we analyze the data using the theory of Sec. II, and compare our data with those of Yu, Gibson, Hunt, and Halperin, who have independently studied NMR in small Pt particles.

II. BACKGROUND

A. Review of the slow beat phenomenon

Consider then the system of Pt nuclear spins ($\vec{I}_j$ for the jth Pt nucleus) in a dc magnetic field $\vec{H}_0$, with the neighboring spins k, coupled by an exchange interaction of the form, $J\vec{I}_j\cdot\vec{I}_k$ (J coupling). For Pt this coupling is much larger than either the dipolar or pseudodipolar interaction. Let there also be a distribution of frequencies ω_{0k} among the spins (inhomogeneous Knight shifts). The situation is then much like that originally analyzed by Hahn.[5]

We irradiate this spin system with two rf pulses to get a spin echo[5,7] (Fig. 1). The first pulse (at time $t=0$) tilts the nuclear magnetization away from the direction of $\vec{H}_0$. The transverse component of magnetization then precesses about $\vec{H}_0$, but, owing to the spread in precession frequencies, the spins get out of phase with one another, and the transverse magnetization consequently decays to zero. The second rf pulse ($t=\tau_d$) inverts the spins. This has the effect of reversing the dephasing process so that during the second time interval τ_d, they come back into phase with one another, and the transverse magnetization reappears at $t=2\tau_d$ like an echo.

The refocusing of the transverse magnetization into an echo is not perfect. For one thing, irreversible processes are always present which eventually destroy the phase memory of the individual spins. Generally, the amplitude S of the spin echo as a function of τ_d decays exponentially. That is

$$S=S_0\exp(-2\tau_d/T_2)\ , \tag{1}$$

where T_2 is the spin-spin relaxation time and S_0 is the amplitude of the spin echo in the limit, $\tau_d \rightarrow 0$.

The J coupling may also affect the spin echo. If neighboring spins are separated in NMR frequency by an amount much greater than J, then we can truncate the form of the J coupling in its "secular" part, $JI_{jz}I_{kz}$. In this case, the J coupling simply causes the NMR frequency of each spin to be shifted by an amount which depends on the z components of its neighboring spins. Thus, for a system of spin $\frac{1}{2}$, a given spin $\vec{I}_j$ which is coupled to a neighboring spin $\vec{I}_k$ is shifted in its NMR frequency ω_{0j} by an amount $\pm\frac{1}{2}J$, depending on whether $\vec{I}_k$ is spin up or down.

Now, if the NMR frequency of $\vec{I}_j$ and $\vec{I}_k$ are close enough together so that the rf pulses can invert both of them simultaneously, then the second rf pulse not only inverts $\vec{I}_j$, but also $\vec{I}_k$. This results in a change in the shift of ω_{0j}, i.e., from $+\frac{1}{2}J$ to $-\frac{1}{2}J$ or from $-\frac{1}{2}J$ to $+\frac{1}{2}J$, depending on the initial z component of $\vec{I}_k$. Thus ω_{0j} has different values during the two intervals τ_d. Consequently, by the end of the second interval τ_d, $\vec{I}_j$ has accumulated a total phase error $J\tau_d$, which diminishes its contribution to the spin echo amplitude by the factor $\cos(J\tau_d)$. If we measure the spin-echo amplitude as a function of τ_d, we observe a "slow beat" of frequency J.

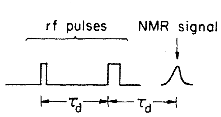

FIG. 1. Spin echo formed by the application of two rf pulses separated by delay times τ_d.

Of course, it is possible for a spin to couple to more than one neighboring spin. This case has been analyzed by Froidevaux and Weger.[8] For example, if $\vec{I}_j$ is coupled to *two* neighboring spins, they cause ω_{0j} to be shifted by either $\pm J$ (spins parallel) or zero (spins antiparallel). The former case causes a phase error $2J\tau_d$ and hence a slow beat of frequency $2J$. Since the neighboring spins may be parallel or antiparallel with equal probability, the contribution of $\vec{I}_j$ to the spin echo is diminished on the average by the factor

$$\tfrac{1}{2}\cos(2J\tau_d)+\tfrac{1}{2}=\cos^2(J\tau_d)\ .$$

Similarly, it is easy to show that if a spin is coupled to r neighboring spins, its contribution to the spin echo is diminished by the factor $\cos^r(J\tau_d)$. Since some spins in a sample may have one neighboring spin, some may have two, some may have three, etc., and, of course, some may have no neighboring spins, we have for the general case,[8]

$$S=S_0\exp(-2\tau_d/T_2)\sum_{r=0}^{\infty}P_r\cos^r(J\tau_d)\ , \tag{2}$$

where P_r is the probability that a spin has r neighboring spins.

We have implied in the above discussion that all spins are close enough in frequency that an rf pulse can invert all of them simultaneously. Generally, an rf pulse of frequency ω and amplitude ω_1 can invert a spin $\vec{I}_j$ of NMR frequency ω_{0j} if

$$|\omega_{0j}-\omega| < \omega_1\ . \tag{3}$$

In a very broad line (large spread in NMR frequencies among the spins), there may be a large fraction of spins which do not satisfy Eq. (3). We can disregard these spins. They cannot participate in the spin echo and also cannot cause slow beats in any of their neighboring spins which do satisfy Eq. (3). We need to only consider the set of spins which satisfy Eq. (3). They participate in the spin echo and also cause slow beats in neighboring spins of the same set. The slow beats are still described by Eq. (2) in this case, if we now define P_r to be the probability that a spin in this set has r neighboring spins which also belong to this set.

B. Small platinum particles

In a metal, polarized conduction-electron spins interact with the nuclear spin $\vec{I}_j$ causing a shift in its NMR frequencies ω_{0j} proportional to the applied magnetic field H_0, the well-known Knight shift. Then

$$\omega_{0j}=(1+K_j)\gamma H_0 , \tag{4}$$

where γH_0 is the NMR frequency of the "bare" nucleus and K_j is the fractional shift in the NMR frequency of spin $\vec{I}_j$.

In bulk Pt metal, the Knight shift is very large. In small Pt particles, surface effects cause large variations in the Knight shift as a function of position in the particle, resulting in a large spread of NMR frequencies among the spins (see paper I). This, of course, is the ideal situation for observing slow beats, providing the difference in NMR frequencies between neighboring spins is not *too* large.

In order to evaluate Eq. (2) for this case, we make the following approximation. Let us define a Knight shift gradient $\vec{\nabla} K_j$ at spin $\vec{I}_j$ such that the Knight shift K_k at any of its neighboring spins $\vec{I}_k$ is given by

$$K_k=K_j+\vec{r}_{jk}\cdot\vec{\nabla} K_j , \tag{5}$$

where $\vec{r}_{jk}$ is the vector from $\vec{I}_j$ to $\vec{I}_k$. Now, if the rf frequency ω is at the NMR frequency ω_{0j} of $\vec{I}_j$ ($\omega=\omega_{0j}$), then the criteria of Eq. (3) becomes, for $K_j \ll 1$,

$$\vec{r}_{jk}\cdot\vec{\nabla} K_j < \omega_1/\omega_{0j} . \tag{6}$$

Only those neighboring spins which satisfy this equation can cause slow beats in $\vec{I}_j$.

If $|\vec{\nabla} K_j|$ is much larger than $\omega_1/a\omega_{0j}$, where a is the distance between nearest neighbors in the crystal lattice, then Eq. (6) can only be satisfied for $\vec{\nabla} K_j$ nearly perpendicular to $\vec{r}_{jk}$, i.e., the neighboring spin must lie near the plane of constant K. In Fig. 2, we plot the directions of $\vec{\nabla} K$ which satisfy Eq. (6) for $|\vec{\nabla} K|a\omega_{0j}/\omega_1=10$. We use the face-centered-cubic lattice of bulk Pt metal in which each atom has twelve nearest neighbors.

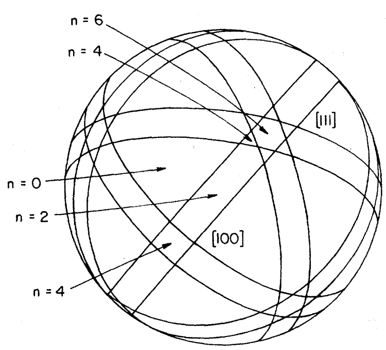

FIG. 2. Directions of $\vec{\nabla} K$ which satisfy Eq. (6) for the twelve nearest neighbors in a face-centered-cubic lattice. The six bands are regions where two neighbors satisfy Eq. (6) simultaneously. Intersections of these bands give rise to regions where four and six neighbors satisfy Eq. (6) simultaneously. This figure is plotted for $|\vec{\nabla} K|a\omega_0/\omega_1=10$.

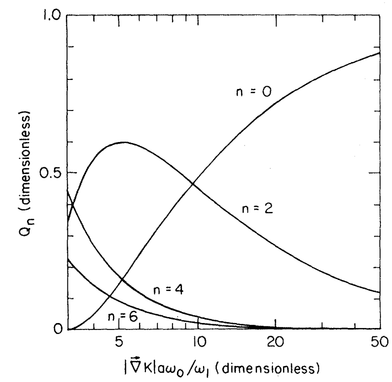

FIG. 3. Probability Q_n that n nearest neighbors satisfy Eq. (6). These are the areas of the respective regions in Fig. 2. For large values of $|\vec{\nabla} K|a\omega_0/\omega_1$, Q_n is given by Eq. (7).

The six "bands" of allowed directions of $\vec{\nabla} K$ arise from the six pairs of nearest neighbors. (Each pair consists of two opposing neighbors which are collinear with $\vec{I}_j$.) Outside these bands, none of the nearest neighbors satisfies Eq. (6). Inside the bands, where they do not overlap each other, only two neighbors satisfy Eq. (6). Where two bands overlap, four neighbors satisfy Eq. (6), and where three bands overlap, six neighbors satisfy Eq. (6). Of course, it is possible, for smaller values of $|\vec{\nabla} K|$, to find directions $\vec{\nabla} K$ for which eight, ten, or even all twelve neighbors satisfy Eq. (6).

At this point, we need to make another approximation. We assume that all directions of $\vec{\nabla} K_j$ with respect to the crystal axes are equally probable. Then the probability Q_n that n nearest neighbors satisfy Eq. (6) is simply the fractional area of the corresponding regions on the surface of the sphere in Fig. 2. For $\omega_1/|\vec{\nabla} K|a\omega_0=\delta \ll 1$, we have

$$\begin{aligned} Q_0&=1-6\delta+8.5\delta^2 , \\ Q_2&=6\delta+14.8\delta^2 , \\ Q_4&=4.1\delta^2 , \end{aligned} \tag{7}$$

and

$$Q_6=2.2\delta^2 .$$

Q_n is zero for all other values of n. Of course, the

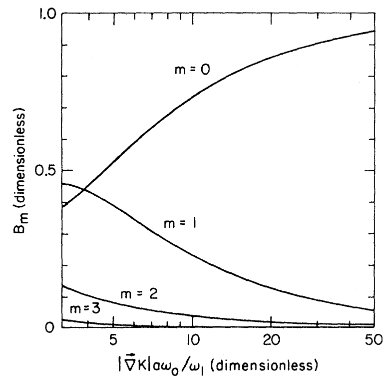

FIG. 4. Fourier coefficients B_m for slow beats in Pt.

areas can also be calculated *exactly* for larger values of δ. The result of these exact calculations is plotted in Fig. 3.

In order to calculate P_r in Eq. (2), we need to take into consideration the isotropic abundance c of ^{195}Pt which is $c = 0.337$. Only neighbors with nuclear spins can produce slow beats. If n neighbors satisfy Eq. (6), the probability A_{nr} that r of them $(r \leq n)$ have spins is simply

$$A_{nr} = \frac{n!}{r!(n-r)!} c^r (1-c)^{n-r} . \tag{8}$$

It clearly follows, then, that

$$P_r = \sum_{n=r}^{12} A_{nr} Q_n . \tag{9}$$

In general, Eq. (2) can be expanded into a Fourier series,

$$S = S_0 \exp(-2\tau_d / T_2) \sum_{m=0}^{12} B_m \cos(mJ\tau_d) . \tag{10}$$

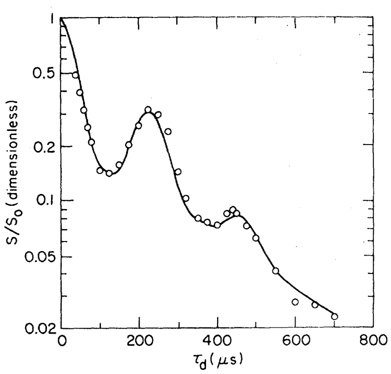

FIG. 5. Spin-echo amplitude S/S_0 at $H_0/\nu_0 = 1.138$ kG/MHz, $\nu_0 = 74$ MHz, and $T = 4.2$ K. Solid line is the best fit to Eq. (10). See Table I.

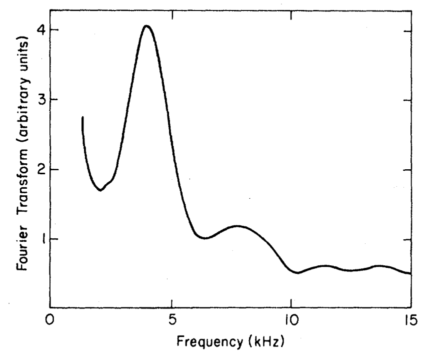

FIG. 6. Fourier transform of the slow beats in Fig. 5. Peaks at the fundamental frequency $J/2\pi$ and its first harmonic $2J/2\pi$ are at about 4 and 8 kHz, respectively.

Using Eqs. (2) and (9), we plot the first four Fourier coefficients B_m as a function of $|\vec{\nabla}K| a\omega_0/\omega_1$ in Fig. 4. In principle, the Fourier coefficients B_m can be extracted from experimentally observed slow beats, and, then, using Fig. 4, we can obtain $|\vec{\nabla}K|$, which gives us information about the *local* variations in the Knight shift.

III. SAMPLE

Our sample consists of small Pt particles supported on alumina. Using electron microscopy, we obtained the size distribution of the Pt particles in this sample (see Fig. 1 in paper I) and found that most of the particles have diameters between 50 and 100 Å. We label this sample Pt-15-*R*. This notation is explained in paper I as well as details of the preparation and characterization of this sample.

The NMR absorption line [see Fig. 5(c) in paper I] was found to be very broad, extending for $H_0/\nu_0 = 1.138$ kG/MHz (the position of ^{195}Pt resonance in bulk Pt metal) to about 1.085 kG/MHz, a width of about 4 kG at $\nu_0 = 74$ MHz. Here, ν_0 is the NMR frequency, related to ω_0 by $\omega_0 = 2\pi\nu_0$.

IV. RESULTS

We measured the amplitude S of the spin echo as a function of the delay time τ_d between the two rf pulses in our sample under various conditions. In Fig. 5, we plot data taken at $\nu_0 = 74$ MHz, temperature $T = 4.2$ K, and $H_0/\nu_0 = 1.38$ kG/MHz. This value of H_0/ν_0 corresponds to the resonance condition in bulk Pt samples. We observe here some very prominant beats. The fundamental frequency of these beats is about 4 kHz, which is the value of

TABLE I. Analysis of slow beats. We obtain T_2, T_{2J}, B_0, B_1, and B_2 by fitting the data to Eq. (11). We then obtain $|\vec{\nabla}K|a\omega_0/\omega_1$ from Fig. 4. Finally, we obtain $|\vec{\nabla}K|$ using $a=2.77$ Å, $\omega_0/2\pi=\nu_0$, $\omega_1/2\pi=90$ kHz at $\nu_0=74$ MHz, and $\omega_1/2\pi=55$ kHz at $\nu_0=8.4$ MHz.

Fig.	ν_0 (MHz)	T (K)	H_0/ν_0 (kG/MHz)	T_2 (μs)	T_{2J} (μs)	B_0	B_1	B_2	$\|\vec{\nabla}K\|a\omega_0/\omega_1$	$\|\vec{\nabla}K\|$ (%/Å)
5	74	4.2	1.138	440	420	0.53	0.39	0.08	4.9	0.22
7	74	77	1.138	110	420	0.48	0.41	0.11	4.3	0.19
8	74	4.2	1.117	800	320	0.77	0.20	0.03	12	0.53
9	8.4	4.2	1.138	320	340	0.57	0.42	0.01	4.5	1.0

$J/2\pi$ determined in dilute alloys of bulk Pt metal of Froidevaux and Weger.[8] If we take the Fourier transform of the data (Fig. 6) we find a corresponding peak at about 4 kHz and we also find a distinct peak at about 8 kHz, indicating a significant contribution from the $m=2$ term in Eq. (10). It would seem reasonable, then, to try to fit the data in Fig. 5 to Eq. (10) using the first three terms, $m=0,1,2$.

Before we attempt that, though, we make one more observation. From the data in Fig. 5, we see that the beats ($m=1,2$ terms) decay faster than the $m=0$ term. This is most likely due to the dipolar and pseudodipolar couplings which act much like a small spread in values of J among the spins, i.e., the strength of the J coupling between neighboring pairs of spins varies slightly from pair to pair in our sample, a function of the orientation of the crystal axes and the particles with respect to $\vec{H}_0$.

Assuming the "spread" in J to be Gaussian, we fit the data in Fig. 5 to

$$S=S_0\exp(-2\tau_d/T_2)\times\{B_0+\exp[-(\tau_d/T_{2J})^2][B_1\cos(J\tau_d)+B_2\cos(2J\tau_d)]\}\ , \tag{11}$$

where T_{2J} is the spin-spin relaxation time associated with the decay of the beats. From the best fit to this equation, we obtained $J/2\pi=4.2$ kHz and values of T_2, T_{2J}, B_0, B_1, and B_2, as shown in Table I. We plot this best fit as a solid line in Fig. 5. Note that the value obtained for T_{2J} corresponds to a spread in $J/2\pi$ of about ± 0.8 kHz about its average value, 4.2 kHz. From Fig. 4, we find that the values of B_0,B_1,B_2 we obtained correspond to $|\vec{\nabla}K|a\omega_0/\omega_1=4.9$. Using $\omega_1/2\pi=90$ kHz and $a=a_0/\sqrt{2}$, where $a_0=3.92$ Å, the lattice constant for Pt metal, we obtain $|\vec{\nabla}K|=(0.22\%)/$Å. This is a *huge* gradient in the Knight shift. Nearest neighbors are shifted from each other in their NMR frequencies on the average by 200 kHz.

These data were taken at $H_0/\nu_0=1.138$ kG/MHz, the position of the Pt resonance in bulk Pt metal. At this position, a prominent peak (the "bulk peak") is observed in the line shape [see Fig. 5(c) of paper I]. We have generally postulated that this peak arises from Pt nuclei which are in the deep interior of the largest particles in the sample. It is there that the electronic environment should most resemble that of bulk Pt metal, thus giving rise to a Knight shift equal to that in bulk Pt metal. However, we see from the slow beats data that even at this position on the line, the Knight shift varies wildly from nucleus to nucleus very much *unlike* bulk Pt. Thus we are forced to conclude that even in particles as large as 100 Å in diameter, there are essentially no Pt nuclei which see themselves in a bulklike environment. This conclusion is supported by the fact that the bulk peak in this sample is much broader than the Pt line shape usually observed in bulk Pt [see Figs. 6(a) and 6(d) in paper I].

We also observe slow beats at 77 K ($\nu_0=74$ MHz and $H_0/\nu_0=1.138$ kG/MHz, as before) which we plot in Fig. 7. Here T_2 is much shorter due to temperature-dependent T_1 effects (see paper II). We find that when we fit this data to Eq. (11), we obtain nearly the same results (except for the effect of temperature on T_2) as we did at 4.2 K at the

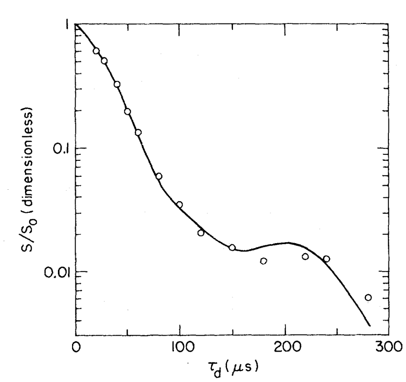

FIG. 7. Spin-echo amplitude S/S_0 at $H_0/\nu_0=1.138$ kG/MHz, $\nu_0=74$ MHz, and $T=77$ K. Solid line is the best fit to Eq. (10). See Table I.

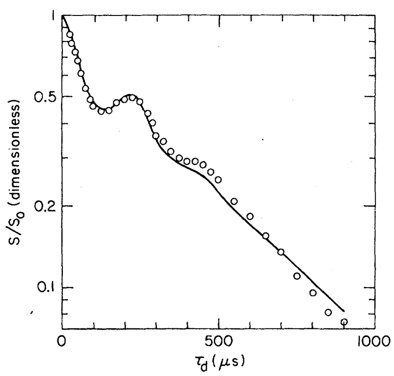

FIG. 8. Spin-echo amplitude S/S_0 at $H_0/\nu_0 = 1.117$ kG/MHz, $\nu_0 = 74$ MHz, and $T = 4.2$ K. Solid line is the best fit to Eq. (10). See Table I.

same position on the line (see Table I). The constants J and $|\vec{\nabla}K|$ are temperature independent, as we would expect.

At positions on the line further down field, the slow beats are weaker. In Fig. 8 we show data taken at $H_0/\nu_0 = 1.117$ kG/MHz ($T = 4.2$ K and $\nu_0 = 74$ MHz). Fitting the data to Eq. (11) and then using Fig. 4, we obtain $|\vec{\nabla}K| = (0.53\%)/\text{Å}$ (see Table I), more than twice the value obtained at 1.138 kG/MHz. This, of course, is the reason that the beats appear weaker. The Knight shift gradient is larger, neighboring spins are shifted further apart in their NMR frequencies, and hence fewer spins can satisfy Eq. (3) and contribute to the slow beat.

This position on the line (1.117 kG/MHz) corresponds to nuclei generally closer to the surface of the Pt particles than those at 1.138 kG/MHz. Conduction electrons are more strongly perturbed, and hence larger spatial variations in the Knight shift are expected, resulting in a larger observed Knight shift gradient $\vec{\nabla}K$. Further down field on the line, $\vec{\nabla}K$ is larger yet, and we hardly observe any slow beats at all.

We have generally asserted that $K = -4\%$ (the bulk peak) at the center of the particles and $K = +1\%$ (the surface peak) at the surface of the particles. There are the values of K at the two extreme ends of the line shape. All other Pt nuclei in the particles take on value of K *between* -4% and $+1\%$. If we were to assume that K is a monotonically increasing function of r, the distance from the center of the particle, then $\vec{\nabla}K$ would point radially outward. The smallest value of $|\vec{\nabla}K|$ is found at the center of the particles ($r = 0$). Using this value, $|\vec{\nabla}K| = (0.22\%)/\text{Å}$, we find that $K = +1\%$ at $r = 23$ Å. Since $|\vec{\nabla}K|$ increases with r, this model predicts that $K = +1\%$ at even smaller values of r than 23 Å.

Since most of the particles in this sample have radii between 25 and 50 Å, we see that this model cannot be correct. K cannot be a monotonically decreasing function of r but must be a spatially oscillating function. Further evidence for this conclusion is also seen in the rather broad peak in the line shape of this sample. The NMR absorption at this peak extends to nearly 0.3% beyond the position of the Pt resonance in bulk Pt. This implies that even near the center of the Pt particles, K oscillates as much as $\pm 0.3\%$ about its value in bulk Pt.

We also took some data at $\nu_0 = 8.4$ MHz ($T = 4.2$ K, $H_0/\nu_0 = 1.138$ kG/MHz) which we plot in Fig. 9. Analyzing the data as before (Table I), we obtain $|\vec{\nabla}K| = (1.0\%)/\text{Å}$, which is very different from the value obtained at $\nu_0 = 74$ MHz at the same position on the line. This is a clear indication that something is wrong with our model for determining $|\vec{\nabla}K|$. Since K is independent of ν_0 (keeping H_0/ν_0 fixed), $\vec{\nabla}K$ must be also. At $H_0/\nu_0 = 1.138$ kG/MHz, $|\vec{\nabla}K|$ must have the *same* value at $\nu_0 = 74$ and 8.4 MHz. Using our model, we obtained at the two frequencies values of $|\vec{\nabla}K|$ that differed by more than a factor of 4, which is well outside the experimental uncertainty of our data.

The difference in field between two neighboring spins $\vec{I}_i$ and $\vec{I}_j$ is given by $|K_i - K_j| H_0$, where K_i and K_j are the Knight shifts of the two spins, respectively. By reducing H_0, we reduce the field difference, and we might therefore expect that some pairs of neighboring spins which at higher H_0 are too far apart in field to contribute to the slow beats might at lower H_0 be close enough together in field to now participate. This would cause more pronounced slow beats at lower H_0 since more pairs of spins participate.

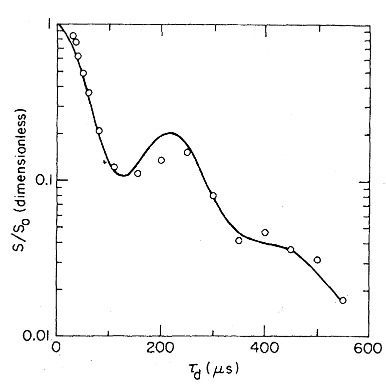

FIG. 9. Spin-echo amplitude S/S_0 at $H_0/\nu_0 = 1.138$ kG/MHz, $\nu_0 = 8.4$ MHz, and $T = 4.2$ K. Solid line is the best fit to Eq. (10). See Table I.

From our data, though, we see that even reducing the field by nearly a factor of 9 seems to have little effect on the slow beats. The slow beats at 8.4 MHz (Fig. 9) look about the same as those at 74 MHz (Fig. 5). In fact, we see in Table I that the Fourier components B_0, B_1, and B_2 are nearly the same for the two cases. This indicates that P_r is also the same, i.e., the same neighboring spins which do not participate in slow beat at 74 MHz also do not at 8.4 MHz. Their difference in Knight shift at 74 MHZ must be so great that even at 8.4 MHz, where that difference is reduced by a factor of 9, they are still not close enough together in field to participate in slow beats.

Our model presented in Sec. II B could be altered to fit this result by assuming that the direction of $\vec{\nabla} K$ with respect to the crystalline axes is highly preferential in certain directions and not equally probable in all directions as we had assumed. This modified model would yield much larger values of $|\vec{\nabla} K|$ than those shown in Table I.

Yu, Gibson, Hunt, and Halperin,[9] also studied small Pt particles at 10 kG and 4.2 K. They observed spin echo decays whose τ_d dependence deviated strongly from exponentials. They analyzed their data using a model similar to that used by Hahn[7,10] to describe the effect on the echo decay of bulk diffusion of nuclei in a gradient of the static field. They proposed that the "diffusion" in Pt is spin diffusion resulting from the pseudoexchange coupling J, and attributed the magnetic field gradient to spatial oscillations of the Knight shift. Their analysis takes the field shift between neighbors to be smaller than J. (In our sample such a small field shift between neighbors occurs only rarely and thus the effects of spin diffusion can be neglected in our analysis.) The different experimental results are readily reconciled if one assumes they had less field inhomogeneity from Knight shift oscillations than we did hence that their signals arose from larger particles than ours.

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