NMR of platinum catalysts. II. Relaxation

Howard E. Rhodes,* Po-Kang Wang, Claus D. Makowka,† Serge L. Rudaz,
Harold T. Stokes,‡ and Charles P. Slichter

*Department of Physics and Materials Research Laboratory, University of Illinois
at Urbana-Champaign, Urbana, Illinois 61801*

J. H. Sinfelt

Exxon Research and Engineering Company, Linden, New Jersey 07036
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The authors report measurement of ^{195}Pt spin-lattice relaxation times T_1 and spin-spin relaxation times T_2 of small particles of Pt supported on alumina. T_1 and T_2 were measured at various static fields H_0, for frequencies ν_0 of 45, 55, and 74 MHz, and at temperatures of 4.2, 77, and 300 K. Though strong functions of H_0/ν_0 at any given ν_0, the relaxation times T_1 and T_2 at fixed H_0/ν_0 are independent of particle size. T_1 is longest at the position (H_0/ν_0) corresponding to the "surface peak" described in paper I (the preceding paper), indicating that conduction-electron spins are largely tied up for surface Pt atoms. The peak in T_1 shifts position with change in surface coating exactly as does the peak in NMR echo amplitude, showing that the change in H_0/ν_0 of the surface peak as a function of surface coating is most likely a chemical shift.

I. INTRODUCTION

In the preceding paper[1] (referred to as paper I), NMR absorption line shapes were presented for several samples of small platinum particles supported on alumina. In this paper, we discuss the nuclear spin-lattice and spin-spin relaxation phenomena which we have observed in some of the samples.[2-7] In particular, we are able to show that most Pt atoms in these samples are "metallic." However, the Pt atoms which are on the surface of the Pt particles and are thus bonded to adsorbed molecules are to a good approximation nonmetallic. We show that the Knight shift for the nuclei of these atoms is vanishingly small, leaving only the chemical shift to determine their NMR frequency.

II. SPIN-LATTICE RELAXATION

Nuclear spins arrive at their thermal equilibrium magnetization by a process called spin-lattice relaxation. This process is usually exponential, with a characteristic time constant T_1, the spin-lattice relaxation time.[8]

We measured T_1 in our samples using a spin-echo technique (Fig. 1). In a spin echo, two rf pulses are applied, separated by a delay time τ_d. At time τ_d after the second pulse, the echo forms spontaneously. The size of the spin-echo signal is directly proportional to the nuclear magnetization lying along the dc magnetic field $\vec{H}_0$ just prior to application of the first pulse. Each spin-echo sequence (pair of rf pulses) destroys the nuclear magnetization along $\vec{H}_0$. The magnetization then grows back towards its equilibrium value until, at a time τ_R later, another spin-echo sequence destroys it. This sequence is repeated so that all spin-echo sequences are separated by the time interval τ_R. The amplitude of each spin echo is thus proportional to the magnetization $M(\tau_R)$ which has been able to grow from zero during the time interval τ_R:

$$M(\tau_R) = M(\infty)[1 - \exp(-\tau_R/T_1)] . \qquad (1)$$

By measuring the spin-echo amplitude for various values of τ_R, we can easily obtain T_1. The equilibrium magnetization $M(\infty)$ is obtained by using a value τ_R a few times T_1.
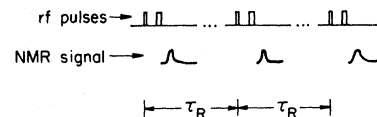
FIG. 1. Pulse sequence for measuring T_1. We vary the repetition time τ_R between each spin echo and obtain T_1 from Eq. (1).

In metals, spin-lattice relaxation proceeds via the Fermi contact interaction with polarized conduction-electron spins.[8] This is the same interaction which causes the Knight shift, as discussed in paper I. In fact, Korringa[9] derived a relation between the Knight shift K and the spin-lattice relaxation time T_1 due to interactions with conduction electrons:

$$T_1 K^2 = \frac{\hbar}{4\pi k_B T} \left[\frac{\gamma_e}{\gamma_n} \right]^2 B , \qquad (2)$$

where k_B is the Boltzmann constant, T is the temperature, and γ_e and γ_n are the gyromagnetic ratios of the electron and nuclear spins, respectively. B is a constant equal to unity for a metal in which many-body effects can be neglected. Pines[10] showed that if many-body effects are included using the random-phase approximation, B is given as

$$B = [\chi^s \rho_0(E_F)/\chi_0^s \rho(E_F)]^2 , \qquad (3)$$

where χ_0^s and $\rho_0(E_F)$ are the conduction electron spin susceptibility and density of states at the Fermi energy E_F without many-body effects, and χ^s and $\rho(E_F)$ are the same quantities including many-body effects. For bulk Pt metal, one finds experimentally that $B = 6$.[11]

We measured T_1 at 77 K as a function of static field H_0 (holding the NMR frequency ν_0 fixed) in three different samples, labeled Pt-15-R, Pt-26-R, and Pt-46-R (Fig. 2). (An explanation of the labeling can be found in paper I.[1]) These samples were found to have dispersions (fraction of Pt atoms which are on the surface of the Pt particles) equal to 15%, 26%, and 46%, respectively. The size distributions of Pt particles in these samples are shown in Fig. 1 of paper I.

From Fig. 2 we see that T_1 is sample independent. This result is consistent with Eq. (2) which predicts that at constant temperature T_1 should be only a function of K. A given position on the NMR line corresponds to a certain Knight shift and consequently to a certain value of T_1, regardless of the particle size. While this result at first glance seems to be nothing more than a verification of the Korringa relation [Eq. (2)], deeper reflection shows that it also tells something new. The Korringa relation was derived for a *homogeneous* solid, whereas in our samples the variation in Knight shift must be enormous between adjacent atomic cells. Thus Fig. 2 shows that the Korringa relation holds cell by cell. A closely related theoretical result has been shown by Zaremba and Zobin,[12] who showed that Knight shift from conduction electrons could be
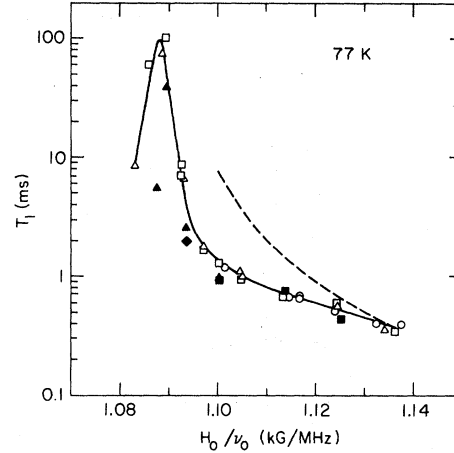

FIG. 2. T_1 at 77 K. $\nu_0 = 74$ MHz for samples Pt-15-R (O), Pt-26-R ($\square$), and Pt-46-R ($\triangle$). $\nu_0 = 55$ MHz for sample Pt-46-R ($\blacklozenge$). $\nu_0 = 45$ MHz for samples Pt-26-R ($\blacksquare$) and Pt-46-R ($\blacktriangle$). The dashed curve is the Korringa relationship [Eq. (2)] normalized at the position of the resonance in the bulk metal, assuming $K = 0$ at the surface peak ($H_0/\nu_0 = 1.089$).

calculated from properties within a single atomic cell. As yet the T_1 has not been derived from such a model, so that a fully local theoretical test of the Korringa relation remains to be established.

The value of T_1 at the position of bulk Pt metal (1.38 kG/MHz) is 0.39 ms, which is in good agreement with the value of T_1 one actually obtains in a sample of bulk Pt metal. As we move across the line to lower fields, the Knight shift K decreases and T_1 increases, as expected. A smaller Knight shift indicates a weaker interaction between nuclei and conduction electrons and hence a weaker spin-lattice relaxation.

Quantitatively, our data do not obey Eq. (2) very well. The dashed line in Fig. 2 is calculated from Eq. (2) with $B = 6$ (the value in bulk Pt) and the assumption that the surface peak in the R samples is at zero Knight shift. This theoretical curve clearly disagrees with the data. One possible explanation for this disagreement is that the quantity B decreases as the Knight shift decreases, corresponding to a decrease in many-body effects. Another possibility is that relaxation by processes that do not contribute to the Knight shift becomes more important at smaller Knight shifts (e.g., relaxation by the classical dipolar coupling between nuclear and electron spins, rather than by the Fermi contact interaction).

At 1.088 kG/MHz we find a peak in T_1 (Fig. 2). At this position, the spin-lattice relaxation is weak-

est, indicating that the conduction-electron spins are tied up in bonds. This situation then prevents the electron spins from being polarized in an applied field leading to zero (or very small) Knight shift. Further down field, T_1 gets shorter again, suggesting that *these* nuclei have a *positive* Knight shift which might arise from an admixture of $6s$ electrons into the $5d$ band as discussed in paper I. (The Knight shift in bulk Pt metal is negative, due to the domination of $5d$ electrons at the Fermi level.) The shortening of T_1 at lower H_0's might also arise from anisotropy in the hyperfine coupling, an effect one should get for the surface Pt atoms. The position of this T_1 peak is at the *same* position as the surface peak in the line shapes discussed in paper I and thus confirms the model presented there: The surface Pt atoms which are bonded to adsorbed molecules are to a good approximation nonmetallic in nature and exhibit effectively zero Knight shift.

We also measured the ν_0 dependence of T_1 as a function of position on the line (Fig. 2). For relaxation due to interactions with conduction electrons, both T_1 and K should be independent of ν_0, keeping H_0/ν_0 constant. In Fig. 2 we see that T_1 is ν_0 independent except near the position of the surface peak. The ν_0 dependence there shows that the environment is nonmetallic. The interaction with conduction electrons is so weak that other relaxation mechanisms (such as paramagnetic impurities) which are not ν_0 independent dominate T_1.

In Fig. 3 we show T_1 data for sample Pt-46-R which had been "cleaned" by a chemical process described in paper I and then exposed to air. (We label this sample Pt-46-air.) The Pt particles in this

sample are probably coated with adsorbed oxygen. As can be seen in the data, the peak in T_1 is·now at a different position (1.095 kG/MHz) than in sample Pt-46-R. As shown in paper I, the surface peak in the line shape also shifted to a new position in this sample. In fact, the new position of the T_1 peak is exactly at the new position of the surface peak. The fact that the T_1 is so long shows that the peak position corresponds to zero Knight shift so that the shift in peak position between samples Pt-46-R and Pt-46-air must be a chemical shift due to a difference in adsorbed molecules bonded to the surface Pt atoms.

We measured T_1 at 4.2 K (Fig. 4) in samples Pt-15-R and Pt-26-R. From Eq. (2) we see that for relaxation in a metal, T_1 is inversely proportional to the temperature T. In Fig. 5 we plot $T_1 T$ as a function of position on the line for data both at 77 and 4.2 K. We see that the Korringa relation ($T_1 T=$const at fixed H_0/ν_0) is very closely obeyed.

III. SPIN-SPIN RELAXATION

In the spin-echo sequence, it is found that the echo amplitude generally decreases as one increases the time τ_d between the pair of rf pulses (Fig. 6). This decrease arises because there are processes which cause the precessing nuclei to lose memory of the phase of their precession. The longer the precession, the greater the loss in phase memory. Often the decay of the echo is exponential in τ_d, proportional to $\exp(-2\tau_d/T_2)$, which defines the spin-spin relaxation time T_2 (see Ref. 8).
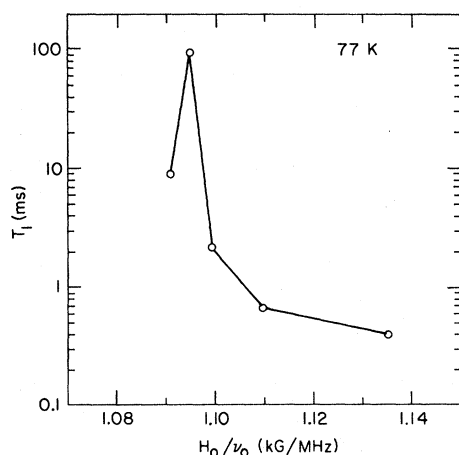

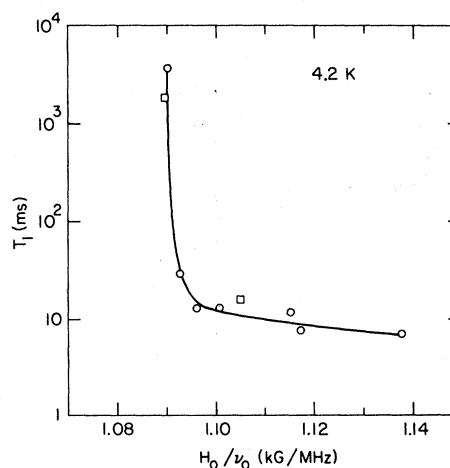FIG. 3. T_1 at 77 K and $\nu_0=74$ MHz for sample Pt-46-air.

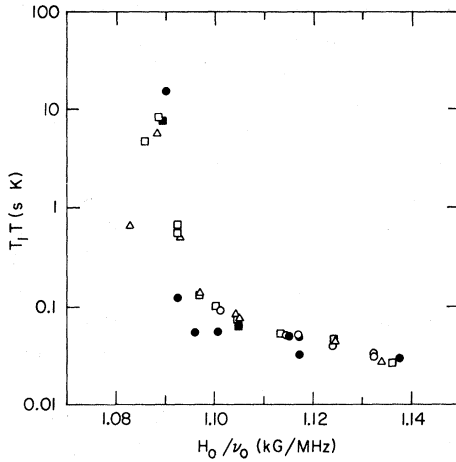FIG. 4. T_1 at 4.2 K and $\nu_0=74$ MHz for samples Pt-15-R (o) and Pt-26-R (□).

FIG. 5. T_1T at 77 K and $\nu_0 = 74$ MHz for samples Pt-15-R (○), Pt-26-R (□), and Pt-46-R (△), and at 4.2 K for samples Pt-15-R (●) and Pt-26-R (■).

We measured T_2 as a function of position on the line for samples Pt-15-R, Pt-26-R, and Pt-46-R at 77 K (Fig. 7). The general shape of the data reminiscent of T_1 (Fig. 2) and suggests that T_2 may be influenced by T_1. In fact, we find that for H_0/ν_0 between 1.10 and 1.14 kG/MHz,

$$\frac{1}{T_2} = \frac{3.6}{T_1} \ . \tag{4}$$

The explanation of Eq. (4) is straightforward in terms of known facts of bulk Pt. Neighboring nuclear spins in Pt couple both directly through their nuclear magnetic moments and indirectly through the intermediary of the conduction-electron spins, the so-called pseudodipolar and pseudoexchange coupling. For bulk Pt, the pseudoexchange coupling (J coupling), of form $J \, \vec{I}_i \cdot \vec{I}_k$ between spins i and k, is the largest of these couplings.

As a result of the J coupling, a given spin I_i sees an additional field due to a neighboring spin I_k. The magnitude of that field is $\pm \frac{1}{2} J / \gamma$, depending on the eigenstate of I_k, spin up or down. [This result is only valid for the case where the difference in
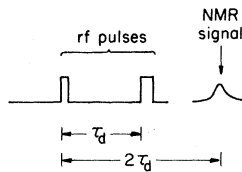

FIG. 6. Pulse sequence for measuring T_2. We vary the delay time τ_d between the pair of pulses. The amplitude of the spin echo is proportional to $\exp(-2\tau_d/T_2)$.
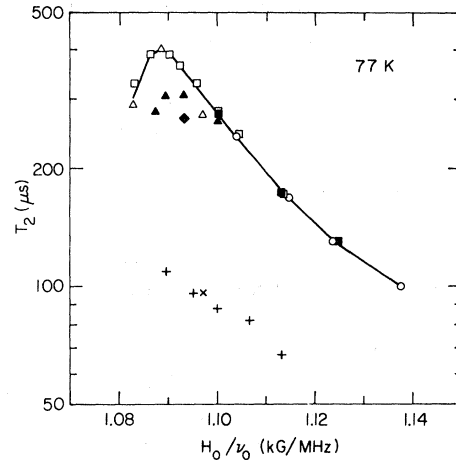

FIG. 7. T_2 at 77 K. $\nu_0 = 74$ MHz for samples Pt-15-R (○), Pt-26-R (□), and Pt-46-R (△). $\nu_0 = 55$ MHz for sample Pt-46-R (◆). $\nu_0 = 45$ MHz for samples Pt-26-R (■) and Pt-46-R (▲). Also, sample Pt-46-H at $\nu_0 = 74$ MHz: 77 K (+) and 300 K (×).

ν_0 between neighboring Pt nuclei is much larger than $J/2\pi$. This is usually the case in our samples because of the large relative Knight shifts between neighbors. See the following paper[13] (paper III) for further discussion of this point.]

T_1 processes cause transitions between the two eigenstates of I_k. This causes a fluctuating field at I_i. It can be shown[14] that the average time τ between such transitions (related to the transition probability W by $\tau = 1/W$) is given by

$$\tau = \frac{1}{2} T_1 \ . \tag{5}$$

After each transition of I_k, the spin I_i loses its phase memory after a time $t \gtrsim J^{-1}$. So, if I_k does not make another transition during this time ($J\tau \gg 1$), we can simply use the Poisson probability function[15] to calculate T_2: The number of spins which are still in phase after a time t is proportional to the probability that the neighbor spin has not made a transition during that time, i.e., $\exp(-t/\tau)$. We can thus easily identify $T_2 = \tau$ in this case and obtain

$$\frac{1}{T_2} = \frac{1}{2T_1} \ . \tag{6}$$

(Note that this calculation is in essence a "strong collision" theory since each flip of a neighbor effectively destroys the phase of I_i.)

If there are Z neighboring spins to I_i, then the probability that any one of its neighbors makes the transition is Z times greater, and we have

$$\frac{1}{T_2} = \frac{Z}{2T_1} \cdot \tag{7}$$

This is the T_2 due to interactions with neighbors. We need to also include the contribution from the T_1 of I_i itself, i.e., the "lifetime broadening."[16] This is precisely T_1^{-1}. We finally obtain

$$\frac{1}{T_2} = \frac{Z+2}{2T_1} \cdot \tag{8}$$

From Eq. (4) we can identify 3.6 with $Z/2 + 1$ which gives us $Z \simeq 5$. Since there are 12 nearest neighbors to any given Pt in a face-centered-cubic crystal and the isotopic abundance of ^{195}Pt is 33.7 at. %, we see that, on the average, there are four neighboring Pt spins which can contribute to T_2. Our result of $Z = 5$ may be an indication of some contribution to T_2 from *next*-nearest neighbors.

We also measured T_2 in sample Pt-15-R at 4.2 K (Fig. 8). Here we found that the data could be described by an equation like Eq. (8), with Z still about 5, if we also added a temperature-independent term $T_2^{(0)}$. We have

$$\frac{1}{T_2} = \frac{Z+2}{2T_1} + \frac{1}{T_2^{(0)}} \cdot \tag{9}$$

We found the best value for $T_2^{(0)}$ to be very close to 1.05 ms which happens to be the low-temperature value of T_2 in bulk Pt metal.[11] [Note that the data point at 1.138 kG/MHz does not fit Eq. (9) very well. This is due to additional relaxation processes which we discuss in paper III.]

Now, with a form like that of Eq. (8) or Eq. (9), we can interpret the T_2 data in terms of an understanding of the T_1 data. For example, T_2 is sample independent and has a peak at the position of the
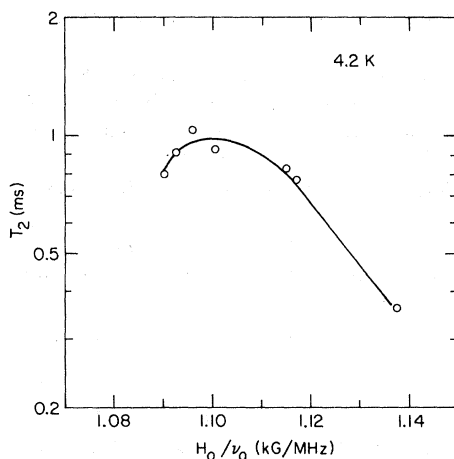
surface peak in the line shape. We also measured the v_0 dependence of T_2 as a function of position on the line (Fig. 7). As with T_1, we find that T_2 is v_0 independent except near the position of the surface peak.

We measured T_2 (Fig. 7) from $H_0/v_0 = 1.089$ to 1.113 kG/MHz in the sample Pt-46-R which had been "cleaned" and then exposed to hydrogen. In this sample, the Pt particles are coated with hydrogen (we label this sample Pt-46-H). As can be seen, coating with hydrogen shortens the Pt T_2 by a factor of about 3. The simplest explanation of this effect is that the ^{1}H magnetic dipole coupling to the ^{195}Pt is responsible. The size of the effect is correct for the first layer of Pt atoms (only an estimate can be made since the size of the ^{195}Pt-^{1}H indirect coupling is not known). The data extend only up to H_0/v_0 of 1.113. From the studies of line shape versus dispersion, we know that such values of H_0/v_0 probably still correspond to only the second or third layer from the surface. If ^{1}H dipolar coupling is shortening the ^{195}Pt T_2, this effect should not arise for H_0/v_0 corresponding to bulk metal. We did not collect data at that part of the line (the sample studied, Pt-46-H, has very weak signals at the bulk metal peak). Another test for the ^{1}H dipolar broadening hypothesis would be to measure the ^{195}Pt T_2 for a surface coated by D_2 rather than by H_2 exposure. If we are correct that the ^{195}Pt T_2 is limited by dipolar coupling to the protons, the fact that the ^{195}Pt T_2 is the same at both 77 K and room temperature places an upper limit on the rate at which H atoms diffuse on the Pt surface at room temperature: The mean time τ_H between diffusion jumps must be longer than the mean time for ^{1}H spins to diffuse by mutual spin flips (roughly $\gamma^2 \hbar / a^3$, where a is the distance between neighboring bonding sites on the surface) approximately 30 μs.

IV. CROSS RELAXATION

Normally, T_1 can also be measured using an "inversion-recovery" technique. This consists of a π pulse which inverts the nuclear magnetization, a wait period of length τ_w, and then a pair of pulses to measure the resulting magnetization via a spin echo. This sequence is repeated, each one separated by a time interval τ_R much greater than T_1. During the wait period, the magnetization grows exponentially towards its equilibrium value with time constant T_1 which can be measured by varying τ_w.

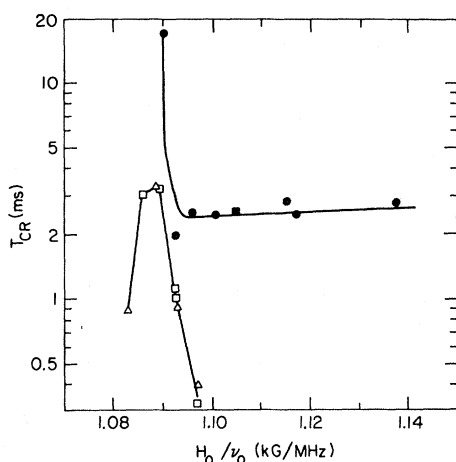When we measured T_1 using this inversion-recovery technique instead of the saturation tech-

FIG. 8. T_2 at 4.2 K for sample Pt-15-R.

FIG. 9. Cross relaxation time τ_{CR} vs H_0/ν_0 for 77 K (open symbols) and 4.2 K (solid symbols). Triangles are Pt-46-R, squares are Pt-26-R, circles are Pt-15-12.

nique described in Sec. II, we found that at some positions on the line the recovery of the magnetization to equilibrium proceeded in two steps: First, a rather fast recovery part way to equilibrium, and then a much slower recovery the rest of the way. We attribute this behavior to cross relaxation. A nuclear spin first rapidly cross relaxes with its neighbors and then, together, they relax to equilibrium with the lattice. Each process is described by a time constant: the first by τ_{CR}, the cross-relaxation time, and the second by T_1, the spin-lattice relaxation time, which we discussed in Sec. II. The

cross-relaxation times τ_{CR} measured at 77 and 4.2 K are shown in Fig. 9.

There are three main reasons why we attribute the fast-component relaxation to cross relaxation and not to just another T_1 process. First, we observe in Fig. 9 that the relaxation time at 4.2 K is shorter than T_1 in bulk Pt metal. It is difficult to conceive of any T_1 process at that temperature which would be stronger than that due to conduction electrons.

Second, under some experimental conditions, we do not observe the fast-component relaxation when we use the saturation technique. This procedure brings all the nuclear spins which participate in the cross relaxation to the *same* magnetization so that no cross relaxation is observed.

Third, the spin-spin relaxation has only one component. If the two-component T_1 relaxation were due to two different kinds of nuclear spins in the sample, each with a different T_1, we would expect them to have a different T_2 also. This would result in a two-component spin-spin relaxation, which we do not observe.

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*Present address: Eastman Kodak, Bldg. 81, Rochester, NY 14650.

†Present address: IBM Thomas J. Watson Research Center, P.O. Box 218, Yorktown Heights, NY 10598.

‡Present address: Department of Physics and Astronomy, Brigham Young University, Provo, UT 84602.

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