Nucleation and Growth Mechanism of Pd/Pt Bimetallic Clusters in Sodium Bis(2-ethylhexyl)sulfosuccinate (AOT) Reverse Micelles as Studied by in Situ X-ray Absorption Spectroscopy

Ching-Hsiang Chen,[†] Bing-Joe Hwang,^{*,†,‡} Guo-Rung Wang,[†] Loka Subramanyam Sarma,[†] Mau-Tsu Tang,[‡] Din-Goa Liu,[‡] and Jyh-Fu Lee[‡]

Nanoelectrochemistry Laboratory, Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei 106, Taiwan, R.O.C.

Received: July 22, 2005; In Final Form: September 14, 2005

We report in situ X-ray absorption spectroscopy (XAS) investigations on the formation of palladium-platinum (Pd/Pt) bimetallic clusters at the early stage within the water-in-oil microemulsion system of water/AOT/*n*-heptane. The reduction of palladium and platinum ions and the formation of corresponding clusters are monitored as a function of dosage of reducing agent, hydrazine (N₂H₅OH). Upon successive addition of the reducing agent, hydrazine (N₂H₅OH), five distinguishable steps are observed in the formation process of Pd/Pt clusters at the early stage. Both in situ X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) analysis for both the Pd K-edge and Pt L_{III}-edge revealed the formation of Pd/Pt bimetallic clusters. A corresponding structural model is proposed for each step to provide a detailed insight into the nucleation and growth mechanism of Pd/Pt bimetallic clusters. We also discussed the atomic distribution of Pd and Pt atoms in Pd/Pt bimetallic clusters based on the calculated XAS structural parameters.

1. Introduction

Bimetallic clusters are of great interest¹ from both scientific and technological perspectives because of the modification of physical and chemical properties not only due to quantum-size effects but also as a result of the combination of different metals.^{2–4} It was observed that the activity and selectivity of the metal catalysts can be drastically influenced by the presence of a second metal component.⁵ In our previous study we demonstrated that the structure of bimetallic catalysts can be significantly influenced by the degree of alloying between the two constituent elements.⁶ Controlling the size and morphology of the metal nanoparticle is a key theme of the nanoparticle research, as it has a strong influence on optical, magnetic, electronic, and catalytic properties of the nanoparticles. Methanol, ethanol, and formic acid are some of the more commonly used alternative fuels, and recent work has shown that formic acid is a particularly attractive candidate for fuel cells.⁷ Such oxidation reaction of the fuel requires a catalyst. Although Pt is the most well-known fuel cell catalyst, in its pure form it suffers from serious surface poisoning due to the adsorption of reaction intermediates. The catalytic activity of Pt surfaces toward formic acid oxidation has been studied in detail,^{8,9} and many infrared spectroscopic studies¹⁰⁻¹² have established that CO adsorption is primarily responsible for surface poisoning. Pd surfaces have been found to possess better catalytic activity toward formic acid oxidation, but a very slow deactivation results in reduced oxidation current.¹³ The Pd/Pt bimetallic system also exhibits a high catalytic ability for hydrogen oxidation.14

Owing to its wide application as a heterogeneous catalyst, we chose the Pd/Pt bimetallic system to study the formation

mechanism. A thorough understanding of the formation mechanism is necessary to control the factors such as size, shape, and surface morphology which govern the catalytic activity of the nanoparticles. Success in either particle design or scalingup also requires a detailed knowledge of the particle formation mechanism. Although a large number of studies were focused on the synthesis and characterization of bimetallic clusters, e.g., Ag/Cu and Au/Cu,¹⁵ Pd/Pt,¹⁶ Pt/Ru,^{17,18} Rh/Pt,¹⁹ and Pd/Au,²⁰ we know of less reports focusing on the formation mechanism of bimetallic clusters at early stages.^{21,22}

One of the methods suitable to study the structure of metal clusters is the in situ X-ray absorption spectroscopy (XAS) comprising both X-ray absorption near-edge (XANES) and extended X-ray absorption fine structure (EXAFS) regions. XANES can reveal the oxidation state and d-band occupancy of a specific atom as well as the size of the metallic cluster,²³ while the local atomic structure can be obtained from the analysis of EXAFS. The XAS technique has been proved as a powerful technique for the characterization of bimetallic catalysts,^{24–26} since it is difficult to obtain structural information on such systems by means of conventional material analysis methods at the early stages. Moreover, due to the change in cluster structure during the course of formation, ex situ techniques such as transmission electron microscopy (TEM) and X-ray diffraction (XRD) have difficulty giving real-time structural information in a reaction atmosphere. Meanwhile, the catalytic activity of bimetallic clusters is strongly influenced by their atomic distribution and structure.⁶ In our previous works, we have successfully evaluated the formation mechanism of monometallic Pt and bimetallic Pt/Cu clusters in AOT reverse microemulsions by in situ XAS.^{21,27}

In line with our ongoing effort to evaluate the formation mechanism of metal nanoparticles, we have aimed here to investigate the formation mechanism of Pd/Pt bimetallic clusters by in situ XAS at the early stages and to provide a detailed

^{*} Corresponding author. Fax: +886-2-27376644. E-mail: bjh@ mail.ntust.edu.tw.

[†] National Taiwan University of Science and Technology.

[‡] National Synchrotron Radiation Research Center, Hsinchu 300, Taiwan.

insight into the nucleation and growth mechanism. In addition, we also attempted to provide detailed information on an atomic distribution and structural model of Pd/Pt bimetallic clusters.

2. Experimental Section

2.1. Preparation of Monometallic Pd Clusters in AOT Reverse Micelles. The monometallic Pd clusters were prepared in a microemulsion containing *n*-heptane as the continuous oil component, water, and surfactant. The surfactant used was 1 M sodium bis(2-ethylhexyl)sulfosuccinate (AOT) (99%). The *n*-heptane and the surfactant were thoroughly mixed, and an aqueous solution of 1 mL of 0.6 M K₂PdCl₄ was subsequently added to form a well-defined microemulsion phase with the Pd complex in the water pool. The volume ratio of the aqueous phase to the organic phase was kept at 1:10. An important parameter characterizing the microemulsion, i.e., the water-tosurfactant molar ratio, $W = \{(water)/(surfactant)\}$, was equal to 5.5 in the present experiment. This microemulsion solution was placed in the liquid cell, which was carefully designed to govern the edge jump, for the in situ XAS measurement. A microemulsion of the same composition of oil, water, and the surfactant that contained the reducing agent was also prepared. The reducing agent solution was composed of 1 M hydrazine (N₂H₅OH) and 1 M sodium hydroxide (NaOH), and their volume ratio was kept at 1:1. An appropriate amount of reducing agent containing microemulsion was then added to the microemulsion containing Pd complex via microsyringe every hour starting at 1 h and ending at 5 h, whereby the Pd complex was reduced to Pd⁰ clusters. As the significant changes in the reduction process occurred during the progressive addition of the reducing agent at 3 h and 5 h, we will show and discuss the XAS data at these two time periods. The final product obtained (at 5 h) in section 2.1 was marked as "S1".

2.2. Preparation of Bimetallic Pd/Pt Clusters in AOT Reverse Micelles. Half of the amount of product S1 was placed in the liquid cell designed for in situ XAS study, and to this an equal amount of the Pt precursor, H_2PtCl_6 emulsion, was introduced (at 6.5 h). Appropriate amounts of reducing agent were then added each hour to form bimetallic Pd/Pt clusters. The H_2PtCl_6 microemulsion solution was prepared by using a procedure similar to that for the preparation of the K_2PdCl_4 microemulsion. The X-ray absorption spectra were recorded at three time intervals, 8.3, 10.3, and 15.3 h, during the progressive addition of the reducing agent. The final product obtained (at 15.3 h) in section 2.2 was marked as "S2". All reactions were carried out at room temperature. Nitrogen gas was purged into the microemulsion system throughout the experiment to prevent the clusters from oxidation by air.

A. In Situ XAS Measurements. The X-ray absorption spectra at the Pd K-edge and the Pt LIII-edge were recorded at beamline BL12B2 at the Spring-8, Japan. The electron storage ring was operated at an energy of 8 GeV and a beam current of 100 mA. A double crystal Si(111) monochromator was employed for energy selection with a resolution $\Delta E/E$ better than 1×10^{-4} at both the Pd K-edge (24352 eV) and the Pt L_{III}-edge (11564 eV). Formation of Pd clusters and the corresponding Pd/Pt bimetallic clusters in reverse micelles proceeded in a homemade cell made with PTFE for in situ XAS study. Two holes were made, one on top of the cell and the other on one side. After placing the liquid sample, the top hole was closed with a Teflon rod to avoid the exposure of the sample to the outer atmosphere. A hollow Teflon rod with a Kapton film cap at one end was inserted into the other hole in the in situ cell. The position of the Teflon rod was adjusted to reach the optimum absorption thickness ($\Delta \mu x \approx 1.0$, $\Delta \mu$ is the absorption edge, x is the thickness of the liquid layer) so that the proper edge jump step could be achieved during the measurements. All of the spectra were recorded at room temperature in a transmission mode. Higher harmonics were eliminated by detuning the double crystal Si(111) monochromator. The incident and transmission X-ray intensities were, respectively, detected by ion chambers that were installed in front of and behind the sample cell. Energy was scanned from 200 eV below the edge to 1000 eV above the edge. Standard compounds, Pd foil and Pt foil for the respective edges, were measured simultaneously by using the third ionization chamber so that energy calibration could be performed scan by scan.

B. XAS Data Analysis. Standard procedures were followed to analyze the EXAFS data. First, the raw absorption spectrum in the pre-edge region was fit to a straight line and the background above the edge was fit using a 11-knot cubic spline function calculated from AUTOBK code. The EXAFS function, χ , was obtained by subtracting the postedge background from the overall absorption and then normalizing with respect to the edge jump step. The normalized $\chi(E)$ was transformed from energy space to k-space. The $\chi(k)$ data were weighted by k^2 in order to compensate for dampening of the XAFS amplitude with increasing k. Subsequently, k^2 -weighted $\chi(k)$ data in the k-space ranging from 3.23 to 10.86 $Å^{-1}$ for the Pd K-edge and from 3.37 to 11.44 \AA^{-1} for the Pt L_{III}-edge were Fourier transformed (FT) to r-space to separate the EXAFS contributions from different coordination shells. A nonlinear least-squares algorithm was applied to curve fitting of EXAFS in r-space between 1.1 and 3.0 Å for the Pd K-edge and between 1.1 and 3.3 Å (without phase correction) for the Pt L_{III} -edge. All the computer programs were implemented in the UWXAFS 3.0 package²⁸ with the backscattering amplitude and the phase shift for the specific atom pairs being theoretically calculated by using FEFF7 code.²⁹ Palladium and platinum foils were employed as references for the Pd-Pd and Pt-Pt bonds. Pd-Pt and Pt-Pd bonds are modeled based on a face-centered cubic (fcc) model containing six Pd and six Pt atoms in symmetric positions. The amplitude reduction factor, S_0^2 , values for Pt and Pd were obtained by analyzing the Pt and Pd foils, respectively, and by fixing coordination numbers in the FEFFIT input file. The S_0^2 values were found to be 0.88 and 0.95 for Pd and Pt, respectively.

3. Results and Discussion

3.1. In Situ XANES and EXAFS at the Pd K-Edge of Pd Clusters. The Pd K-edge XANES spectra of the Pd microemulsion system as a function of dosage of reducing agent, hydrazine, are shown in Figure 1a. In the XANES spectra the absorption transition in the pre-edge region is a 1s to 4d dipole forbidden transition according to the selection rule, $\Delta l = 1$ and $\Delta j = 1$, where *l* is the orbital angular momentum and *j* is the total angular moment of the local density of states.³⁰ The absorption threshold resonance, called the white line, appearing between 24360 and 24380 eV corresponds to the electronic transitions that arise from the 1s state to the unoccupied 4p states above the Fermi level. The second (24385 eV) and third (24435 eV) peaks correspond to $1s \rightarrow dp$ and $1s \rightarrow dsp$ transitions, respectively. This white line intensity is sensitive to changes in electron occupancy in the valance orbital and ligand field environments of the absorber.^{31,32} Hence, it can be used to calculate the density of the unoccupied states and the changes in the oxidation state of the Pd absorber. As can be seen from Figure 1a, the white line intensity of the initial Pd^{2+} solution gradually decreases as the reducing agent amount increases from 0 to 61.6×10^{-5} mol, indicating the progressive reduction of



Figure 1. (a) XANES spectra and (b) FT of k^2 -weighted EXAFS data at the Pd K-edge of the Pd microemulsion system as a function of hydrazine dosage.

Pd²⁺ to Pd⁰. The Fourier transformed (FT) k^2 -weighted EXAFS spectra ($\Delta k = 3.23 - 10.86 \text{ Å}^{-1}$) of Pd microemulsions, as shown in Figure 1b, reveal a peak between 1.5 and 2.0 Å corresponding to the Pd–Cl bond. After the addition of 26.4 × 10⁻⁵ mol of N₂H₅OH at 3 h, the magnitude of the Pd–Cl bond is decreased and a new peak appears between 2.0 and 3.0 Å related to the Pd–Pd bond, indicating that [PdCl₄]^{2–} ions were reduced and Pd clusters were formed directly without any intermediate. The corresponding chemical reaction can be written as follows:

$$N_2H_5OH + 2[PdCl_4]^{2^-} + 4OH^- \rightarrow N_2 + 2Pd^0 + 8Cl^- + 5H_2O$$
 (1)

In the final step, after the addition of 61.6×10^{-5} mol of N₂H₅OH at 5 h, the FT peak corresponding to the Pd–Cl bond disappears completely and the magnitude of the Pd–Pd bond



Figure 2. Normalized XANES spectra near the Pd K-edge of the Pd/ Pt bimetallic microemulsion system.

increases. This implies that all of the palladium ions were completely reduced to Pd^0 and were transformed to Pd clusters. The Pd clusters thus obtained are marked as "S1".

3.2. In Situ XANES at the Pd K-Edge and the Pt L_{III} -Edge of Bimetallic Pd/Pt Clusters. Half of the amount of Pd clusters labeled as "S1" is placed in the liquid cell, and an equal amount of the H₂PtCl₆ emulsion is introduced into the system. The Pd K-edge XANES spectra of the bimetallic Pd/Pt microemulsion system as a function of dosage of the reducing agent are shown in Figure 2. After the addition of the Pt⁴⁺ microemulsion, the white line intensity increases slightly due to the oxidation of the Pd clusters. The white line energy position is found to be at 24375 eV, and it matches closely with the white line energy position of the PdCl species of the [PdCl₄]²⁻ microemulsion, indicating the formation of Pd-Cl species in this state. There was also a change in the white line energy position with addition of 132.2×10^{-5} mol of the reducing agent at 8.3 h, indicating the generation of new species around the Pd core atoms. We also checked the white line energy position which is found to be at 24367 eV, and it is close to the white line energy position of the Pd-OH species of the Pd-(H₂O)₄²⁺ complex.³³ These observations indicate that one of the possibilities is the formation of Pd-OH species. After further addition of the reducing agent, the white line intensity decreases, indicating that the oxidation state of the Pd core ions is reduced to Pd⁰.

The Pt L_{III}-edge XANES spectra of the bimetallic Pd/Pt microemulsion system as a function of the reducing agent dosage are shown in Figure 3. The white line at the Pt L_{III}-edge is an absorption threshold resonance, attributed to the electronic transition from the $2p_{3/2}$ state to unoccupied states above the Fermi level and is sensitive to changes in electron occupancy in the valence orbitals of the absorber.³¹ Hence, changes in the white line intensity have been directly related to the density of unoccupied 5d states and indicate the changes in the oxidation state of the Pt absorber. As can be seen from the Figure 3 inset, the decrease of the white line intensity with an increase in the reducing agent dosage suggested the decrease in the electron vacancy. Generally speaking, the lower the white line intensity,



Figure 3. Normalized XANES spectra near the Pt L_{III} -edge of the Pd/Pt bimetallic microemulsion system.

the higher the electron density and the lower the oxidation state. Hence, changes in the white line intensity may be regarded as an indication of the reduction of the Pt core ions in the bimetallic Pd/Pt microemulsion system (labeled as "S2").

3.3. In Situ EXAFS at the Pd K-Edge and the Pt $L_{\rm III}\text{-}$ Edge of Bimetallic Pd/Pt Clusters. At the beginning of the experiment, half of the amount of Pd clusters "S1" is placed in the liquid cell. The Fourier transformed k^2 -weighted EXAFS spectra ($\Delta k = 3.23 - 10.86$ Å⁻¹) at the Pd K-edge of the bimetallic Pd/Pt microemulsion system, as shown in Figure 4, demonstrate a peak between 1.5 and 2.0 Å corresponding to the Pd-Pd bond. After the addition of the Pt4+ microemulsion into the system, the magnitude of the Pd-Pd bond is decreased and a new peak corresponding to the Pd-Cl bond, which has a magnitude comparable with the Pd K-edge k^2 -weighted EXAFS spectrum of the [PdCl4]²⁻ microemulsion, appears between 2.0 and 3.0 Å. The magnitude of Pd-Cl bond is decreased and a new peak related to the Pd-OH bond is formed after the addition of 132.2×10^{-5} mol of reducing agent at 8.3 h. We have fitted the Pd-OH bond with the FEFF7 software package, and the data are shown in Table 2. Upon further addition of 229×10^{-5} mol of the reducing agent at 10.3 h, the magnitude of the Pd-OH bond decreases and the magnitudes of not only the Pd-Pd bond but also the Pd-Pt bond increase. However, after the addition of 325.8×10^{-5} mol of reducing agent at 15.3 h, the magnitudes of both the Pd-Pd and Pd-Pt bonds increase and the Pd-OH bond completely disappears. The imaginary part and absolute magnitude of the Fourier transform of the Pd K-edge for the final sample S2 and for the Pd foil were compared in the top and bottom panels, respectively, of Figure 5.

The Fourier transformed k^2 -weighted EXAFS spectra ($\Delta k = 3.37 - 11.44$ Å⁻¹) at the Pt L_{III}-edge of the bimetallic Pd/Pt microemulsion system are shown in Figure 6. A peak appears in the range of 1.8–2.1 Å when the Pt⁴⁺ microemulsion is added



Figure 4. FT-EXAFS spectra at the Pd K-edge of the bimetallic Pd/ Pt system as a function of reducing agent dosage.

into the system, and it is ascribed to the Pt-Cl bond, consistent with our previous work.²⁷ After the addition of 132.2×10^{-5} mol of reducing agent at 9 h, the magnitude of the Pt-Cl bond decreased gradually and a new peak appeared at around 1.4-1.8 Å, which is attributed to the Pt-OH bond and increases in magnitude. Further addition of 229×10^{-5} mol of reducing agent at 11.5 h decreases the magnitude of the Pt-OH bond and increases the magnitudes of both the Pt-Pt and the Pt-Pd bonds. After the addition of reducing agent to 325.8×10^{-5} mol at 15.8 h, the magnitudes of both the Pt-Pt and Pt-Pd bonds are increased and the magnitude of the Pt-OH bond is decreased. As can be seen from both Figures 4 and 6, there are two peaks between 2.0 and 3.5 Å in both the Pd K-edge and the Pt L_{III}-edge FT-EXAFS spectra, and this shows that the bonding distances of Pd-Pd and Pt-Pt from the spectra of S2 are larger than those of the Pd foil and the Pt foil, respectively. This indicates that not only Pd atoms but also Pt atoms contain heteroatomic bonds at the state of S2. We have shown the imaginary and absolute magnitudes of Fourier transforms of sample S2 and the Pt foil in the top and bottom panels, respectively, of Figure 7. The k^2 -weighted EXAFS spectra recorded at the Pd K-edge and the Pt LIII-edge for the state of S2 are shown in Figures 8 and 9, respectively. The EXAFS oscillation frequencies at both the Pd K-edge and the Pt L_{III}edge of S2 are different from those of Pd and Pt foils, indicating the existence of correlations between Pd and Pt. All these observations indicate that the metallic ions have been reduced and form Pd/Pt bimetallic clusters.

3.4. Formation Mechanism of Monometallic Pd Nanoclusters in Reverse Microemulsions. The structural parameters (coordination number *N*, bond distance *R*, Debye–Waller factor σ^2 , inner potential shift ΔE_0) derived from the Pd K-edge EXAFS data analysis are shown in Table 1. The coordination number N_{Pd-C1} is found to be 3.86 in the absence of reducing agent. However, after the addition of 26.4×10^{-5} mol of N₂H₅-OH at 3 h, N_{Pd-C1} is decreased to 1.89 and contributions from Pd coordination begin to appear (N_{Pd-Pd} , 4.14), indicating that Pd clusters are formed. Further increasing hydrazine dosage

TABLE 1: Structural Parameters Derived from the Pd K-Edge EXAFS Data Analysis of the Pd Microemulsion System with Various Contents of Reducing Agent^a

| amount of N2H5OH (mol) | time (h) | shell | Ν | R_j (Å) | $\sigma_{j}^{2} (\times 10^{-3} \text{\AA}^{2})$ | $\Delta E_0 ({ m eV})$ | R factor | |
|---|----------|-------|--------------|---------------|--|------------------------|----------|--|
| 0 | 0 | Pd-Cl | 3.86 (0.13) | 2.136 (0.003) | 3.1 (0.3) | 2.13 (0.40) | 0.00041 | |
| 26.4×10^{-5} | 3 | Pd-Cl | 1.89 (0.02) | 2.304 (0.001) | 3.5 (0.1) | 0.13 (0.11) | 0.00009 | |
| | | Pd-Pd | 4.14 (0.04) | 2.739 (0.001) | 4.7 (0.1) | -2.11(0.08) | | |
| $61.6 \times 10^{-5} (S1)$ | 5 | Pd-Pd | 8.20 (0.32) | 2.733 (0.003) | 5.4 (0.5) | -5.01(0.28) | 0.00293 | |
| Pd foil | | Pd-Pd | 12.00 (0.50) | 2.748 (0.004) | 6.4 (0.6) | 2.51 (0.29) | 0.00433 | |
| ^{<i>a</i>} N = coordination number, R (Å) = bonding distance, σ^2 (Å ²) = Debye–Waller factor, and ΔE_0 (eV) = inner potential shift. | | | | | | | | |

 TABLE 2: Structural Parameters Derived from the Pd K-Edge EXAFS Data Analysis of the Pd/Pt Bimetallic Clusters System with Various Contents of Reducing Agent

| amount of N2H5OH (mol) | time (h) | shell | Ν | R_j (Å) | $\sigma_{j}^{2}(\times 10^{-3} \text{ Å}^{2})$ | $\Delta E_0 ({ m eV})$ | R factor |
|-------------------------------|----------|-------|--------------|---------------|--|------------------------|----------|
| S1 | 5 | Pd-Pd | 8.20 (0.32) | 2.733 (0.003) | 5.4 (0.5) | -5.01 (0.28) | 0.00293 |
| add equal mole of Pt emulsion | 6.5 | Pd-Cl | 3.89 (0.08) | 2.303 (0.002) | 2.3 (0.4) | 2.26 (0.26) | 0.00171 |
| | | Pd-Pd | 0.90 (0.51) | 2.825 (0.030) | 5.6 (0.6) | 16.87 (3.11) | |
| 132.2×10^{-5} | 8.3 | Pd-OH | 3.51 (0.32) | 2.058 (0.008) | 4.9 (1.3) | 2.09 (1.13) | 0.03147 |
| | | Pd-Pd | 0.90 (0.61) | 2.821 (0.037) | 6.5 (0.4) | 18.01 (5.09) | |
| 229×10^{-5} | 10.3 | Pd-OH | 2.31 (0.08) | 2.068 (0.003) | 9.5 (0.7) | 1.06 (0.31) | 0.00118 |
| | | Pd-Pd | 2.88 (0.11) | 2.744 (0.003) | 3.3 (0.4) | -5.69(0.24) | |
| | | Pd-Pt | 1.01 (0.12) | 2.811 (0.010) | 0.0 (1.2) | 6.34 (1.03) | |
| $325.8 \times 10^{-5} (S2)$ | 15.3 | Pd-Pd | 5.24 (0.28) | 2.747 (0.003) | 4.8 (0.4) | -3.56(0.52) | 0.00526 |
| | | Pd-Pt | 4.42 (0.61) | 2.750 (0.010) | 7.8 (1.2) | -4.00 (1.21) | |
| Pd foil | — | Pd-Pd | 12.00 (0.50) | 2.738 (0.004) | 6.4 (0.6) | 2.51 (0.29) | 0.00433 |

^{*a*} N = coordination number, R (Å) = bonding distance, σ^2 (Å²) = Debye–Waller factor, and ΔE_0 (eV) = inner potential shift.

leads to a decrease in Pd–Cl coordination and an increase in Pd–Pd coordination, indicating growth of Pd clusters. Metallic nanoparticles synthesized from the reverse micellar solutions are expected to possess a uniform morphology.^{21,27} The coordination number derived from XAS is a nonlinear function of particle diameter, and it has been widely used in EXAFS analysis to determine the size of the nanoparticle.^{34–37} In the present study, the Pd–Pd coordination number is found to be 8.2 with the reducing agent dosage of 61.6×10^{-5} mol at 5 h, indicating that the particle diameter of Pd clusters is between 1.5 and 2.0 nm.

The formation mechanism of Pd nanoclusters is proposed to be step by step in this work based on the XAS results, and a schematic representation of the formation process is depicted in Scheme 1. Two reaction steps of three stages were proposed in this model. In the initial stage (see stage A, Scheme 1), the microemulsion system contains Pd^{2+} ions, Cl^- ions, and the SO_3^- groups of the AOT surfactant. After the addition of 26.4 $\times 10^{-5}$ mol of N₂H₅OH (reduction reaction, I), Pd²⁺ ions are reduced to Pd⁰ nuclei through intermicellar exchange processes (see stage B in the model).^{38,39} After the addition of 61.6 $\times 10^{-5}$ mol of N₂H₅OH (reduction reaction, II), Pd²⁺ ions are completely reduced to Pd⁰ clusters (see stage C in the model).

3.5. Reaction between Monometallic Pd Nanoclusters and Pt^{4+} **Ions in Reverse Micelles.** The XAS structural parameters derived from the Pd K-edge and Pt L_{III}-edge EXAFS data analysis and are shown in Tables 2 and 3, respectively. The coordination number of Cl around Pd and Pt is found to be 3.89 and 4.10, respectively, after the addition of the Pt⁴⁺ micro-emulsion into the system. And we also found the coordination number of Pd around Pd as 0.9 at this stage, indicating that the Pd clusters are not completely dissolved and the Pd clusters



Figure 5. Imaginary part and real magnitude of Fourier transforms of the Pd K-edge for the sample S2 (top panel) and for the Pd foil (bottom panel).



Figure 6. FT-EXAFS spectra at the Pt L_{III} -edge of the bimetallic Pd/ Pt microemulsion system as a function of reducing agent dosage.



Figure 7. Imaginary part and real magnitude of Fourier transforms of the Pt L_{III} -edge for the sample S2 (top panel) and for the Pt foil (bottom panel).



Figure 8. *k*²-weighted EXAFS spectra recorded for Pd/Pt bimetallic clusters (S2) at the Pd K-edge.



Figure 9. k^2 -weighted EXAFS spectra recorded for Pd/Pt bimetallic clusters (S2) at the Pt L_{III}-edge.

would be the nuclei in the system. Because there are two kinds of chemical species, $PdCl_4^{2-}$ and Pd clusters, dispersed in the solution, a two-shell model was used to fit the k^2 -weighted

EXAFS data of the Pd K-edge. Since XAS is an average technique, the coordination numbers of both the Pd-Cl bond and the Pd-Pd bond would be averaged out. Therefore, the real coordination number of the Pd-Pd bond would be underestimated. This implies that the coordination number of the Pd-Pd bond should be larger than 0.9 at this stage. The reason the Pd cluster would not be dissolved is that the equilibrium potential (E_0) of the electrochemical reaction [PtCl₆]²⁻ + 2e⁻ \rightarrow [PtCl₄]²⁻ + 2Cl⁻, 0.680 V/NHE, is slightly higher than the equilibrium potential of the electrochemical reaction [PdCl₄]²⁻ $+ 2e^{-} \rightarrow Pd^{0} + 4Cl^{-}, 0.591 \text{ V/NHE}.^{40}$ The higher equilibrium potential for the platinum complex indicates that the palladium clusters would be oxidized and formed a local corrosion cell in the system. The real coordination number of Cl around Pt in the system is lower than that in H₂PtCl₆ solution, whose coordination number is $6,^{27}$ indicating that the electrochemical reaction, $[PdCl_4]^{2-} + 2e^- \rightarrow Pd^0 + 4Cl^-$, has proceeded with the addition of the Pt⁴⁺ microemulsion into the system in order to keep the charge balance. After the addition of 132.2×10^{-5} mol of reducing agent at 8.3 h, the coordination of Cl around Pd disappears and the coordination of OH around Pd appears and its value is found to be 3.51 without changing the valance state, as shown in Figure 2. This is consistent with the formation of a $[Pd(OH)_4]^{2-}$ complex. We also found a decrease in coordination of Cl around Pt to 2.17, and coordination of OH around Pt is observed and its value is 1.17 at 9 h. These observations are consistent with the formation of $[Pt(OH)_4]^{2-}$ species.²⁷ This indicates that the ligand exchange rate in palladium is higher than that in platinum. Further addition of 229×10^{-5} mol of reducing agent decreased the coordination of OH around both Pd and Pt and generated the Pt-Pd bond and the Pd-Pd bond, indicating the existence of correlations between Pd and Pt. The corresponding reactions could be written as follows:

$$N_{2}H_{5}OH + [Pd(OH)_{4}]^{2^{-}} + [Pt(OH)_{4}]^{2^{-}} + 4H^{+} \rightarrow Pd^{0}/Pt^{0} + N_{2} + 6H_{2} + 3H_{2}O$$
 (2)

Finally, N_{Pd-Pd} and N_{Pd-Pt} are found to be 5.24 and 4.42, respectively, from the Pd K-edge and N_{Pt-Pd} and N_{Pt-Pt} are found to be 2.91 and 6.78, respectively, from the Pt L_{III}-edge with the addition of 325.8 × 10⁻⁵ mol of reducing agent.

We checked the reliability of the Pd–Pt and Pt–Pd bonds of the bimetallic Pd/Pt clusters at the state of S2 by comparing the FEFF theoretical fit with the back-transformed experimental EXAFS data of the Pd K-edge and the Pt L_{III}-edge, as shown in Figures 10 and 11, respectively. The two-shell theoretical fit (hollow circle line) matches closely with the back-transformed experimental data (solid square line); this good fit quality indicates that not only the Pd–Pd and Pt–Pd bonds at Pd K-edge but also the Pd–Pt and Pt–Pt bonds at the Pt L_{III}-edge are reliable.

3.6. Formation Mechanism of Pd/Pt Nanoclusters in Reverse Microemulsions. From the XAS results discussed above a model is proposed for the formation of bimetallic Pd/ Pt clusters in microemulsions, as shown in Scheme 2. Four reaction steps of five stages are proposed in this model. Initially, the Pd cluster "S1" is placed in the liquid cell. The microemulsion system contains Pd⁰ clusters and the SO₃⁻ group of the AOT surfactant (see stage A, Scheme 2). After the addition of the Pt⁴⁺ microemulsion in the first reaction step (reaction, I), some of the Pd⁰ is dissolved and forms Pd–Cl bonds, and [PtCl₄]^{2–} complexes are formed in order to keep the charge balance (see stage B, Scheme 2). The coordination numbers N_{Pd-Cl} and N_{Pt-Cl} are found to be 3.81 and 4.10. We also found

SCHEME 1: Model Proposed for the Formation Mechanism of Monometallic Pd Clusters at Early Stages



 $\label{eq:Reaction} \begin{array}{l} \mbox{Reaction (I): } 26.4 \ x \ 10^{-5} \ \mbox{mol} \ N_2H_5OH, \ 3 \ \mbox{hr} \\ \mbox{Reaction (II): } 61.6 \ x \ 10^{-5} \ \mbox{mol} \ N_2H_5OH, \ 5 \ \mbox{hr} \ \mbox{(Product S1)} \end{array}$

TABLE 3: Structural Parameters Derived from the Pt L_{III} -edge EXAFS Data Analysis of the Pd/Pt Bimetallic Clusters System with Various Contents of Reducing Agent

| amount of N2H5OH (mol) | time (h) | shell | Ν | R_j (Å) | $\sigma_{j}^{2} (\times 10^{-3} \text{ Å}^{2})$ | $\Delta E_0 ({ m eV})$ | R factor |
|-------------------------------|----------|-------|--------------|---------------|---|------------------------|----------|
| add equal mole of Pt emulsion | 7 | Pt-Cl | 4.10 (0.17) | 2.317 (0.007) | 2.2 (0.4) | 9.15 (0.50) | 0.00641 |
| 132.2×10^{-5} | 9 | Pt-OH | 1.17 (0.11) | 1.914 (0.007) | 1.6 (0.9) | -5.73 (1.35) | 0.00499 |
| | | Pt-Cl | 2.17 (0.09) | 2.317 (0.003) | 4.2 (0.4) | 9.03 (0.57) | |
| 229×10^{-5} | 11.5 | Pt-OH | 0.88 (0.14) | 1.914 (0.011) | 4.3 (1.3) | -11.69 (1.71) | 0.01384 |
| | | Pt-Pd | 1.99 (0.29) | 2.671 (0.011) | 8.8 (1.5) | 0.24 (1.36) | |
| | | Pt-Pt | 6.64 (0.38) | 2.672 (0.004) | 7.3 (0.5) | -2.29 (0.63) | |
| $325.8 \times 10^{-5} (S2)$ | 15.8 | Pt-Pd | 2.91 (0.32) | 2.748 (0.007) | 6.3 (0.8) | 2.96 (1.21) | 0.02235 |
| | | Pt-Pt | 6.78 (0.58) | 2.758 (0.006) | 7.3 (0.8) | 3.74 (0.89) | |
| Pt foil | | Pt-Pt | 12.00 (0.29) | 2.778 (0.007) | 4.8 (0.2) | 6.48 (0.27) | 0.00394 |

^{*a*} N = coordination number, R (Å) = bonding distance, σ^2 (Å²) = Debye–Waller factor, and ΔE_0 (eV) = inner potential shift.

the coordination number N_{Pd-Pd} is 0.9. After the addition of 132.2 × 10⁻⁵ mol of N₂H₅OH in the second reaction step (reaction, II), both the Pd–Cl and Pt–Cl bonds are transferred to Pd–OH and Pt–OH, respectively (stage C, Scheme 2). This indicates that the ligand exchange happens in both metallic cores. Reverse micelles in solution will exchange the contents of their cores via both fusion and redispersion processes.^{41–44} As a result, the reduction of metal ions within the cores of reverse micelles can result in the growth of nanosized metal particles. This particle growth within the cores of the reverse micelles the exchange process occurs when micelles collide because of the Brownian motion and the attractive forces

between the micelles. These collisions result in fusion of the reverse micelles, an exchange of the contents within the cores, and a redispersion of the micelles. $^{41-44}$ Further the addition of 229 × 10⁻⁵ mol of N₂H₅OH (reaction III) resulted in the formation of Pd–Pt and Pt–Pd bonds. We found N_{Pd-Pt} and N_{Pt-Pd} to be 1.01 and 1.99, respectively, at this stage; however, Pt–OH is still found in reaction III (see stage D, Scheme 2). At the final step (reaction IV, formation of pure Pd/Pt bimetallic clusters), N_{Pd-Pd} and N_{Pd-Pt} are found to be 5.24 and 4.42, respectively. From the Pt L_{III}-edge, N_{Pt-Pd} and N_{Pt-Pt} are found to be 2.91 and 6.78, respectively. In the resulting Pd/Pt clusters, the total coordination number of Pd and Pt around absorbing "Pd" atoms ($N_{Pd-Pd} + N_{Pd-Pt}$, 9.66) is almost similar to the total



Figure 10. Two-shell fits with back-Fourier transformed experimental EXAFS data for Pd/Pt bimetallic clusters (S2) at the Pd K-edge.



Figure 11. Two-shell fits with back-Fourier transformed experimental EXAFS data for Pd/Pt bimetallic clusters (S2) at the Pt L_{III}-edge.

SCHEME 2: Model Proposed for the Formation Mechanism of Bimetallic Pd-Pt Clusters at Early Stages



Reaction (I): Addition of H_2PtCl_6 microemulsion to Pd⁰ clusters, 6.5 hrs Reaction (II): Addition of 132.2 x 10⁻⁵ mol N₂H₅OH, 8.3 hrs Reaction (III): Addition of 229 x 10⁻⁵ mol N₂H₅OH, 10.3 hrs Reaction (IV): Addition of 325 x 10⁻⁵ mol N₂H₅OH (Product S2), 15.3 hrs

coordination number of Pd and Pt around "Pt" atoms ($N_{Pt-Pd} + N_{Pt-Pt}$, 9.69), indicating that the size of the Pd/Pt cluster is between 2.5 and 3.0 nm.³⁴

3.7. Composition, Atomic Distribution, and Nanostructure of Pd/Pt Bimetallic Clusters. The composition of the Pd/Pt cluster is calculated from XAS by measuring the edge jump ($\Delta\mu x$) at the Pd K-edge and the Pt L_{III}-edge, and it is found that the atomic ratio of Pd:Pt is 1.2:1 (Pd_{1.2}Pt). Recently, we have explored an XAS based methodology to determine the alloying extent or atomic distribution of bimetallic nanoparticles.⁶ We have applied this methodology to the Pd/Pt system investigated here. Basically, in the case of a homogeneous system for which the core of the cluster is composed of *N* atoms of A (NA) and the surface is made of *N* atoms of B (NB), the total coordination ($N_{AA} + N_{AB}$) is equal to 12 for the A atom and less than 12 for the B atom.⁴⁵ More generally, we have the following relationships:

$$N_{AA} + N_{AB} = 12 > N_{BA} + N_{BB}, \quad (NA)N_{AB} = (NB)N_{BA},$$

 $\sigma_{AB} = \sigma_{BA}, \quad R_{AB} = R_{BA} \quad (3)$

In the case of the Pd/Pt bimetallic clusters of the present study, the coordination numbers of the Pd and Pt atoms around the Pd atom are found to be 5.24 and 4.42, respectively, and the total coordination number of $A = \sum N_{Pd-i}$ is 9.66. The coordination

tion numbers of the Pd and Pt atoms around the Pt atom are determined as 2.91 and 6.78, respectively, and the total coordination number of $B = \sum N_{Pt-i}$ is 9.69. The total coordination numbers of A and B are almost the same, indicating that the particle size in both "Pd" and "Pt" is the same. From these values the structural parameters P_{obs} ($N_{Pd-Pt}/\sum N_{Pd-i}$) and R_{obs} $(N_{\text{Pt-Pd}}/\Sigma N_{\text{Pt-i}})$, which can be used to determine the atomic distribution, were calculated as 0.46 and 0.30, respectively. The higher value of P_{obs} , 0.46, indicates the higher extent of atomic dispersion of "Pd" atoms when compared to Pt. In other words, the segregation of Pt atoms is more serious, as the lower value of R_{obs} , 0.30, suggests. It is also interesting to discuss the extent of metallic interaction based on the alloy extent of "Pd" and "Pt". In this case, the homoatomic coordination number of "Pd" atoms around the Pd core is slightly higher than the heteroatomic coordination number of "Pt" atoms around the Pd core, indicating that there are probably two regions on the local Pd cluster structure. One of the regions looks like Pt-Pd alloy particles stacked together, and the other is a Pd-Pd stack. As we can see in Tables 2 and 3, the time taken for Cl ligand transfer to OH ligand in the case of the Pd is shorter than the time taken for the same in the case of the Pt. The higher ligand exchange rate implies that the Pd-OH can be first reduced to Pd⁰ and that it would be in the core of the bimetallic cluster. From the Pt L_{III}-edge XAS, we found that the homoatomic



Figure 12. Schematic representation of the Pd/Pt bimetallic nanoparticle structure based on EXAFS results.

coordination number of "Pt" atoms around the Pt core is higher than the heteroatomic coordination number of "Pd" atoms around the Pt core. Again, this indicates that two regions exist on the local Pt cluster structure. On the basis of our understanding of the results, we expect the Pt–Pt stacked region is larger than the Pd–Pt stacked region. All these observations indicate that there are three stacking regions in the clusters, viz. Pd– Pd/Pd–Pt/Pt–Pt. We also defined two structural parameters to describe the bimetallic nanoparticle structure. The extent of alloying of element "Pd" (J_{Pd}) and element "Pt" (J_{Pt}) for 1.2:1 Pd/Pt bimetallic NPs can be calculated quantitatively by using eqs 4 and 5, respectively.

$$J_{\rm Pd} = \frac{P_{\rm obs}}{P_{\rm random}} \times 100\% \tag{4}$$

$$J_{\rm Pt} = \frac{R_{\rm obs}}{R_{\rm random}} \times 100\%$$
 (5)

 P_{random} and R_{random} can be taken as 0.455 and 0.545, respectively, for perfect alloyed bimetallic NPs if the atomic ratio of "Pd" and "Pt" is 1.2:1. The structural parameters J_{Pd} and J_{Pt} were calculated as 101.1% and 55.0%, respectively. The higher J_{Pd} value indicates the higher alloying level around the Pd atoms. Similarly, the lower J_{Pt} value indicates the lower alloying level around the Pt and larger segregation of Pt. In the resulting structural model, as shown in Figure 12, the Pt atoms are partially segregated and rich in the shell region, the Pd—Pt alloy atoms are preferentially located in the core region, and the Pd atoms act as nuclei to form bimetallic Pd/Pt clusters.

4. Conclusion

The formation mechanism of Pd/Pt bimetallic clusters in AOT reverse microemulsions was investigated by in situ X-ray absorption spectroscopy. Analysis of the XAS data at the Pd K-edge and the Pt L_{III} -edge led us to conclude that the Pt atoms are partially segregated and rich in the shell region, the Pd-Pt alloy atoms are preferentially located in the core region, and the Pd atoms act as nuclei to form the bimetallic Pd/Pt clusters in reverse micelles. For all the formation steps possible, structural models were proposed to account for the XAS observations. We believe that the knowledge gained through the understanding of the cluster formation mechanism would definitely help us to design nanoparticles with the desired size, shape, and morphology. The work presented here is worked-

out in this direction and provides a detailed insight into the mechanism and growth of Pd/Pt bimetallic clusters.

Acknowledgment. The financial support from the National Science Council (under Contract Numbers NSC93-2811-E-011-008, NSC94-2214-E-011-010, and NSC94-2120-M-011-002), the National Taiwan University of Science and Technology, and the National Synchrotron Radiation Research Center (NSRRC) is gratefully acknowledged.

References and Notes

(1) Zhou, B.; Hermans, S.; Somorjai, G. A. Nanotechnology in Catalysis; Kluwer Academic/Plenum Publishers: New York, 2004.

(2) Sinfelt, J. H. Bimetallic Catalysts-Discoveries, Concepts, and Applications: Exxon Monograph; Wiley: New York, 1983.

- (3) Sinfelt, J. H. J. Catal. 1973, 29, 308.
- (4) Sinfelt, J. H. Acc. Chem. Res. 1989, 20, 134.
- (5) Burch, R.; Garla, L. C. J. Catal. 1981, 71, 360.

(6) Hwang, B.-J.; Sarma, L. S.; Chen, J.-M.; Chen, C.-H.; Shih, S.-C.; Wang, G.-R.; Liu, D.-G.; Lee, J.-F.; Tang, M.-T. J. Am. Chem. Soc. 2005, 127, 11140.

(7) Rice, C.; Ha, S.; Masel, R. I.; Waszczuk, P.; Wieckowski, A.; Barnard, T. J. Power Sources **2002**, 111, 83.

- (8) Lu, G.-Q.; Crown, A.; Wieckowski, A. J. Phys. Chem. B 1999, 103, 9700.
 - (9) Jiang, J.; Kucernak, A. J. Electroanal. Chem. 2002, 520, 64.
 - (10) Chang, S. C.; Ho, Y.; Weaver, M. J. Surf. Sci. 1992, 265, 81.
- (11) Iwasita, T.; Xia, X.; Herrero, E.; Liess, H. D. Langmuir 1996, 12, 4260.
- (12) Arenz, M.; Stamenkovic, V.; Schmidt, T. J.; Wandelt, K.; Ross, P. N.; Markovic, N. M. *Phys. Chem. Chem. Phys.* **2003**, *5*, 4242.
- (13) Pavese, A. G.; Solis, V. M.; Giordano, M. C. Electrochem. Acta 1995, 142, 3399.
- (14) Stonehart, P. J. Hydrogen Energy 1984, 9, 921.
- (15) Meitzner, G.; Via, G. H.; Lytle, F. W.; Sinfelt, J. H. J. Chem. Phys. **1985**, 83, 4793.
- (16) Harada, M.; Asakura, K.; Ueki, Y.; Toshima, N. J. Phys. Chem. 1992, 96, 9730.
- (17) McBreen, J.; Mukerjee, S. J. Electrochem. Soc. 1995, 142, 3399.
 (18) Hills, C. W.; Nashner, M. S.; Frenkel, A. I.; Shapley, J. R.; Nuzzo, R. G. Langmuir 1999, 15, 690.
 - (19) Cimini, F.; Prins, R. J. Phys. Chem. B 1997, 101, 5285.
 - (1) Chinn, P., Phils, R. & P. Phys. Chem. B 1999, 101, 5265.
 (20) Reifsnyder, S. N.; Lamb, H. H. J. Phys. Chem. B 1999, 103, 321.
 - (21) Hwang, B.-J.; Tsai, Y.-W.; Sarma, L. S.; Tseng, Y. L.; Liu, D. G.;
- Lee, J. F. J. Phys. Chem. B 2004, 108, 10427.
- (22) Bazin, D.; Triconnet, A.; Moureaux, P. Nuclear Instrum. Methods Phys. Res., Sect. B 1995, 97, 41.
- (23) (a) Bazin, D.; Rehr, J. J. J. Phys. Chem. B 2003, 107, 12398. (b) Bazin, D.; Sayers, D.; Rehr, J. J.; Mottet, C. J. Phys. Chem. B 1997, 101, 5332.
- (24) Frelink, T.; Visscher, W.; van Veen, J. A. R. Surf. Sci. 1995, 335, 353.
- (25) Sinfelt, J. H.; Via, G. H.; Lytle, F. W. Catal. Rev. Sci. Eng. 1984, 26, 81.
- (26) Bazin, D. C.; Sayers, D. A.; Rehr, J. J. J. Phys. Chem. B 1997, 101, 11040.
- (27) Tsai, Y.-W.; Tseng, Y. L.; Sarma, L. S.; Liu, D.-G.; Lee, J.-F.; Hwang, B.-J. J. Phys. Chem. B 2004, 108, 8148.
- (28) Stern, E. A.; Newville, M.; Ravel, B.; Yacoby, Y.; Haskel, D. *Physica B* **1995**, 208&209, 117.
- (29) Zabinsky, S. I.; Rehr, J. J.; Ankudinov, A. L.; Albers, R. C.; Eller, M. J. Phys. Rev. B 1995, 52, 2995.
 - (30) Choi, S. J.; Kang, S. K. Catal. Today 2004, 93, 561.
 - (31) Horsely, J. A. J. Chem. Phys. 1982, 76, 1451.
- (32) Koningsberger, D. C.; Prins, R. In Principles, Application, Techniques of EXAFS, SEXAFS, and XANES; Wiley: New York, 1988.
- (33) Purans, J.; Fourest, B.; Cannes, C.; Sladkov, V.; David, F.; Venanlt, L.; Lecomte, M. J. Phys. Chem. B 2005, 109, 11074.
- (34) Frenkel, A. I.; Hills, C. W.; Nuzzo, R. G. J. Phys. Chem. B 2001, 105, 12689.
- (35) Shibata, T.; Bunker, B. A.; Zhang, Z.; Meisel, D.; Vardeman, C. F., II; Gezelter, D. J. Am. Chem. Soc. 2002, 124, 11989.
- (36) Via, G. H.; Sinfelt, J. H.; Lytle, F. W. J. Chem. Phys. 1979, 71, 690.
 (37) Greegor, R. B.; Lytle, F. W. J. Catal. 1980, 63, 476.
- (38) Hirai, T.; Sato, H.; Komasawa, I. Ind. Eng. Chem. Res. 1994, 33, 3262.
- (39) Bagwe, R. P.; Khilar, K. C. Langmuir 1997, 13, 6432.

(40) *CRC Handbook of Chemistry and Physics*, 80th ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1999–2000.

- (41) Joshi, S. S.; Patil, S. F.; Iyer, V.; Mahumuni, S. Nanostruct. Mater. 1998, 10, 1135.
- (42) Petit, C.; Jain, T. K.; Billoudet, F.; Pileni, M. P. Langmuir 1994, 10, 4446.
- (43) Towey, T. F.; Khan-Lodhi, A.; Robinson, B. H. J. Chem. Soc., Faraday Trans. 1990, 86, 3757.
- (44) Natarajan, U.; Handique, K.; Mehra, A.; Bellare, J. R.; Khilar, K. C. *Langmuir* **1996**, *12*, 2670.
- (45) Moonen, J.; Slot, J.; Lefferts, L.; Bazin, D.; Dexpert, H. *Physica B* **1995**, 208–209, 689.