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Electronic and structural investigations of palladium clusters by x-ray absorption near-edge structure and extended x-ray absorption fine-structure spectroscopies

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Palladium metal clusters with an average diameter of 14 Å embedded in a carbon matrix have been studied by synchrotron-radiation x-ray absorption measurements. The data analysis of the $L_{2,3}$ edge (p-d transitions) shows (a) a strong reduction of the absolute value of the absorption compared to the bulk, (b) a shift towards higher binding energies of about 2 eV, and (c) a broadening of the same structures. We explain these effects as mainly due to a change of the d density of states at the Fermi level, since the L_1 edge (s-p transitions) does not show similar effects. The extended x-ray absorption fine-structure analysis reveals an important increase of about 3% of the first-nearest-neighbor distance, in contrast with other metals which show a lattice contraction.

I. INTRODUCTION

Recently there has been a great amount of experimental work on the lattice-parameter variations occurring in small metal clusters and their technological implications.[1-5] Many investigators have reported moderate lattice contraction, of the order of a few percent, in various metal-substrate systems and under various experimental conditions.[2,3,6]

In *in situ* transmission electron diffraction (TED) studies, Heinemann and Poppa[4] and Garmon and Doering[7] recently have found a lattice expansion for Pd metal particles deposited on mica and MgO single-crystal substrates. Possible origins of this expansion have been attributed to a change from an icosahedral structure to a fcc crystal structure during the particle coalescence,[4] and to substrate-induced lattice strain.[7]

In order to verify the previous hypotheses on Pd clusters we have performed a structural investigation by means of the extended x-ray absorption fine-structure (EXAFS) technique which has a local sensitivity greater than the diffraction methods.[2] Our structural studies on Pd clusters have been investigated with x-ray absorption near-edge structure (XANES).

It has been previously observed that the filled d band of Pd clusters moves toward higher binding energy as the cluster size decreases.[8,9] The XANES technique,[10,11] on the other hand, probes the partial unfilled density of states (DOS), and is thus a suitable method to monitor any change in the electronic structure above E_F (Fermi level). Our data analyses have shown (a) a significant change of the empty d states of Pd clusters compared to the bulk, (b) an fcc-like structure for the smallest clusters with no more than three coordination shells, and (c) a nearest-neighbor distance 3% greater than in the bulk.

II. SAMPLE PREPARATION AND EXPERIMENTAL DETAILS

Palladium clusters embedded in a carbon matrix were deposited *in vacuo* at a pressure of about 10^{-8} Torr, by cosputtering of C and Pd onto a 6-μm-thick Mylar sheet. An equivalent thickness d of about 1 μm of Pd, to obtain the optimum metal thickness for x-ray measurements, was deposited at a rate of about 0.15 nm/min. The micrographs and the diffraction patterns of a very thin film with 200 Å of Pd, deposited in the same previous conditions and covered with small MgO single crystals (used as reference), were taken by a Philips EM-430 electron microscope operating at 250 keV. The micrographs examined by light optical densitometry showed that the film contained only Pd clusters with a mean diameter of about 14 Å. The measurements of the (311) plane spacing from the diffraction patterns showed a lattice-parameter expansion of about 3% of the previous cluster and an expansion of about 1.5% of the clusters with mean diameter of about 150 Å.

The x-ray absorption measurements were performed using the continuum x-ray spectrum emitted by the ADONE storage ring of the Frascati synchrotron-radiation facility operating at an energy of 1.2 GeV and a typical electron current of 50 mA. The spectra were taken at room temperature.

III. EXPERIMENTAL RESULTS

Figures 1 and 2 show the x-ray absorption near-edge structures of the Pd bulk and cluster around the L_3, L_2, and L_1 excitation at 3173, 3331, and 3605 eV, respectively. The line shapes in the spectra show important differences in going from pure Pd to Pd clusters. For the $L_{2,3}$ edges these differences may be summarized as (a) a shift of the main structure of about 2 eV toward the higher binding energies, and (b) a sizeable broadening of the main peak. As shown the spectra are normalized arbitrarily per Pd atom. The total absorption ad (a is the absorption coefficient) of the Pd cluster shows, relative to the bulk, a similar strength of the $L_{2,3}$ white lines, although the white line for the L_2 edge is enhanced. It should be stressed, however, that once the thickness of the samples is taken into account, the absorption coefficient a of the cluster is much smaller (a factor of 10) than that of the bulk.

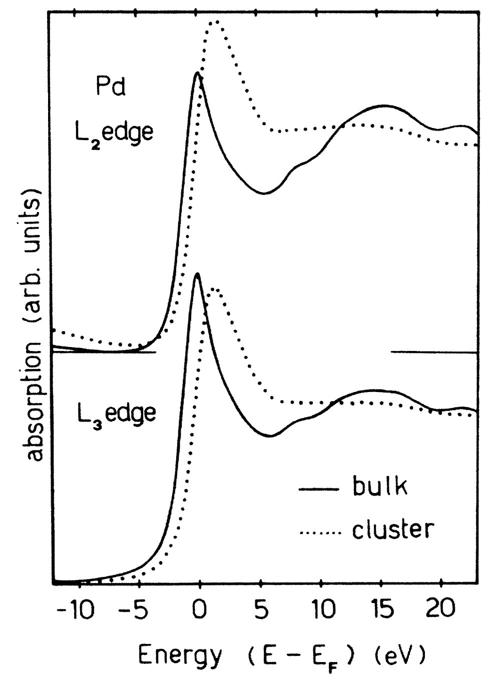

FIG. 1. $L_{2,3}$ absorption edge for bulk (solid curve) and Pd cluster with a mean diameter of 14 Å (dotted curve). All spectra are referred to the Fermi level [for the bulk E_F corresponds to the energy of the white line maximum (Refs. 10 and 11)].

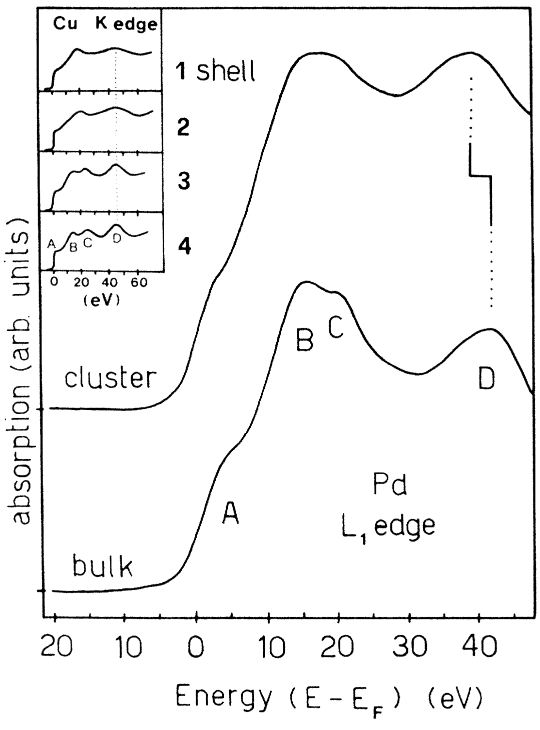

FIG. 2. L_{I} absorption edge for Pd cluster (upper curve) and Pd bulk (lower curve). E_F for the bulk corresponds to the energy of the first inflection point (Refs. 10 and 11). The inset shows the Cu K edge (Ref. 12) computed for increasing number of shells.

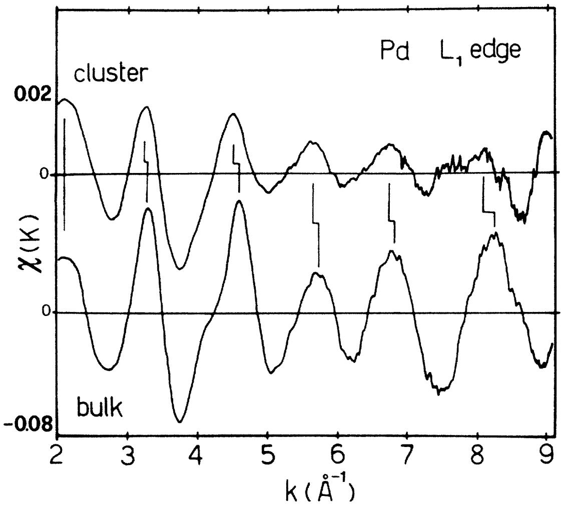

FIG. 3. EXAFS spectrum of the L_{I} edge for Pd cluster (upper curve) and Pd bulk (lower curve).

The XANES of the L_{I} edge for Pd bulk displays four structures labeled A,B,C,D. Qualitatively the spectrum of the cluster is quite similar to that of the bulk, but quantitatively the features B and C are unresolved, while the D peak is shifted toward low binding energy. Figure 3 shows the L_{I} EXAFS oscillations[13] for pure Pd and the Pd cluster. All the cluster EXAFS features show an increasing shift as a function of wave vector k.

Figure 4 shows the Fourier transform [$F(R)$] of the EXAFS spectra of Fig. 3. The $F(R)$ displays different structures in the range 1–6 Å, which are related to the neighbor's positions in real space. The first structure in $F(R)$ at 1.7 Å is due to the Ramsawer-Townsend modulation of the backscattering amplitude.[14] The second structure in $F(R)$ corresponds to the distance of the nearest

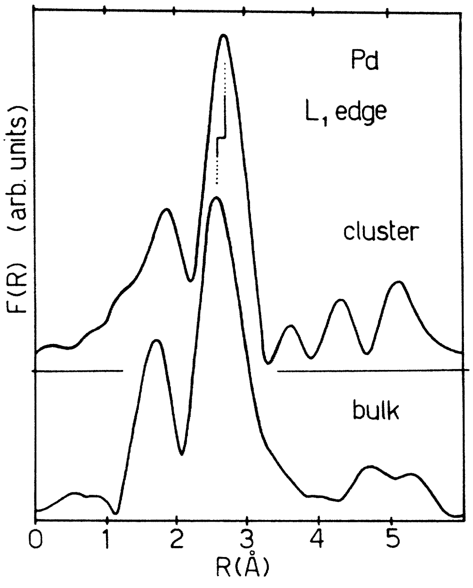

FIG. 4. Fourier transform of the EXAFS spectra of Fig. 3 for Pd cluster (upper curve) and Pd bulk (lower curve).

neighbors. For the Pd bulk this peak is located at 2.58 ± 0.02 Å which corresponds, after the EXAFS phase-shift correction,[13,14] to the inverse square root of the fcc lattice parameter ($R_j = 2.76$ Å).

The direct comparison between $F(R)$ for the bulk and for the Pd cluster shows a lattice parameter expansion of about 3% in the nearest-neighbor position, in excellent agreement with our TED observation. The same conclusion may be inferred from the analysis of the L_2 EXAFS edges.

IV. DISCUSSION

A. XANES region

The empty d DOS above E_F can be monitored in the 0–50 eV energy range beyond the onset of the absorption edge with XANES from the $L_{2,3}$ edges ($2p \rightarrow \epsilon d$ final states). The filled DOS can be monitored with photoemission. As reported by x-ray (XPS) and ultraviolet photoemission spectroscopy (UPS) results of the d states of clusters,[8,9,15,16] there is a shift to higher binding energy relative to the d states in the bulk. This is the same trend as observed here for the unfilled d DOS of the Pd clusters.

In order to understand the origin of the $L_{2,3}$ edge shifts we must consider several possible mechanisms: (i) changes in initial-state configuration,[8] (ii) differences in final-state screening,[8,11] and (iii) differences in density of states.

All these effects should play, in principle, an important role when a core electron is excited into the levels of a very small cluster which resemble those of an isolated atom. Moreover, the previous effects should depend on the very low density of conduction electrons at E_F which screen the deep core hole in the cluster. One of the most important observations of the present work is that the L_1 edge, corresponding to $2s \rightarrow \epsilon p$ transitions, does not show a sizeable shift as observed for the $L_{2,3}$ edges. We may conclude that the Fermi level E_F does not shift also for $L_{2,3}$ thresholds when going from the bulk to the Pd cluster. As a consequence, the absence of E_F shifts rules out effect (i) as the one responsible for the $L_{2,3}$ main feature shift. In fact, if initial-state effects were responsible for the corresponding atomic-level differences between the cluster and the bulk, the $L_{2,3}$ and L_1 edges would shift together, thus showing the same energy shift. Mechanism (ii) cannot be invoked to explain the absorption $L_{2,3}$ edge shifts, despite its current use in explaining the origin of the XPS core-level shifts in clusters deposited on poorly conducting substrates.[17] This consideration is justified because the screening mechanisms underlying the XANES and XPS techniques are different. The XANES edge energy is that required to excite an electron from a core level to the first unoccupied orbital, just above E_F. This state corresponds to the screened or relaxed energy, requiring no further screening charge from the support. The XPS energy, on the other hand, is that required to eject a core electron well into the continuum. The positive charge left behind must now be screened from electrons from the support. If the support is poorly conducting, then the system is left in an excited state with a net positive charge.[12,18] As a result, final-state effects play an important role in the XPS core-level measurements where the degree of screening is not complete, while in the XANES spectra (relaxed system), the extra-atomic relaxation should be relatively unimportant.

Thus the shifts observed in $L_{2,3}$ XANES spectra for the Pd cluster and the low value of their absolute absorption coefficient compared to the bulk can be seen as a simple change of the d DOS at E_F.

In similar XANES studies on Pd Clusters, Mason[8] reported a shift of the $L_{2,3}$ structures (similar to our results) and an enhancement, both of which he attributed to an effect of changes in initial-state configuration. We believe, on the basis of our results, that these conclusions are misleading for two reasons. First, in going from pure Pd to Pd clusters, he took into account the absorption per atom and not the absorption coefficient. Second, the position of E_F in the cluster can be reliably determined only through a joint analysis of $L_{2,3}$ and L_1 edges.

The information on the local geometries of the Pd clusters can be obtained from the L_1 edge analysis. Greaves, Durham, Diacon, and Quinn,[12] using the multiple scattering calculation, have reproduced all the features in the Cu K-edge XANES region (inset of Fig. 2).

The L_1 edge of the Pd bulk shows a one-to-one comparison with the computed Cu K edge when at least four coordination shells are included. The comparison between our absorption coefficient spectra of the Pd cluster with the computed K edge of Cu suggests that (i) the maximum number of shells involved is not greater than three (at this number, in fact, the computed Cu K edge shows a separation between B and C structures), and (ii) the cluster structure is still fcc-like coordinated. However, other coordinated crystalline structures for the cluster (like icosahedral), which display a diffraction pattern similar to that of fcc, cannot be ruled out without a complete XANES calculation.[19] Moreover, the expansion of the lattice parameter occurring in the Pd clusters can be deduced from our XANES spectra just looking at the narrowing distances between B (C) and D structures. It should be noted, in fact, that in the computed Cu K edge, where no lattice-parameter expansion is considered, the D peak is located at the same energy position (dotted line in the inset of Fig. 2).

B. EXAFS region

The analysis of the EXAFS spectra around the L_1 and L_2 edges has been carried out on the basis of the well-established theoretical $\chi(k)$ function[13] which describes the modulation superimposed on the smooth atomic absorption above the edge onset.

The $F(R)$ Fourier transform of $\chi(k)$ shows different peaks corresponding to the different shells surrounding the absorbing atom.

For this reason the EXAFS technique has been used as a powerful tool for giving direct local structure information around a selected atom.

From our analysis we obtained, for the first coordination shell, an expanded interatomic distance of 2.68 ± 0.02 Å. This is the first EXAFS observation of a lattice-parameter expansion for clusters.

Previous EXAFS results[2,3,6,20–22] performed on Au, Ag, Cu, Ni, Pt, and Fe have shown a sizeable contraction of order of a few percent in going from bulk to small metal clusters. This contraction has been commonly attributed to a force effect exerted by the surface stress.[22]

Recently Heinemann and Poppa[4] have suggested, on the basis of TED analysis, that in the case of Pd clusters an important expansion of the interatomic distance may occur. To explain this disagreement, the previous authors interpreted the expansion as due to the icosahedral structure of the smallest clusters, which evolves toward the fcc structure when the particle diameter increases.

We may conclude then that our structural results are in good agreement with Heinemann and Poppa's diffraction measurements. On the basis of their suggestions, a quantitative EXAFS interpretation of the lattice expansion of Pd clusters is in progress.

V. CONCLUSION

We have shown that the XANES and EXAFS studies of both pure Pd and Pd clusters embedded in a carbon matrix give information on the crystalline parameter and the evolution of the d valence band in going from the bulk to the Pd cluster. We have found, for Pd clusters relative to the Pd bulk, (a) a decrease of the absolute absorption coefficient for L_2,L_3 edge white lines, (b) no shift of E_F from the analysis of the L_1 edge, and (c) an important expansion of the lattice parameter. Results (a) and (b) are attributed to the d-band shift which causes a depletion of the d density of states above E_F, while observation (c) may be tentatively interpreted as a change of crystalline structure from fcc to icosahedral for the smallest Pd clusters.

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