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## Experimental and theoretical investigation of correlation effects in aggregates of Ni and Pd as a function of their size

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**Abstract.** An experimental investigation of the UPS and Auger spectra of Ni and Pd aggregates on a SiO<sub>2</sub> substrate is presented. It shows that whereas the width of the UPS spectra increases for both metals when the crystallite size increases, the width of their Auger spectra increases for Pd and decreases for Ni. This was unexpected, since both types of spectra should broaden with the cluster size due to an increasing average coordination number. This surprising observation can be interpreted theoretically as being due to a monotonic change in electronic configuration between the atom and the solid, modifying their Auger linewidth via electronic correlation effects.

### 1. Introduction

Metal aggregates lie between isolated atoms and condensed matter. Therefore their electronic and chemical properties may exhibit a specific behaviour. During the last decade, the importance of this new field has increased considerably both for the understanding of fundamental problems like the transition from the atomic (insulator) to the bulk metallic (conductor) state and for applications such as heterogeneous catalysis and crystal growth processes.

The aim of this paper is to study by means of Auger (AES) and ultraviolet photoelectron spectroscopy (UPS) the variation with the size of the electronic structure of small clusters of nickel and palladium, prepared by an atomic beam technique. Indeed, when the size of the cluster increases, one expects, for instance, a broadening of the valence density-of-states which should be seen in UPS. Moreover, since the electronic configuration in the atom is different from that in the corresponding solid, this configuration should vary continuously between these two limits as a function of the size.

This variation should appear in the corresponding evolution of the width of the AES spectra since it has been shown that this width depends strongly on the number of d holes, at least for metals with an almost filled d band (Tréglia *et al* 1981, hereafter

referred to as I). In this respect, the comparison of Ni and Pd should be particularly interesting since their respective numbers of d holes vary in an opposite way when going from the atom to the metal.

In § 2 we describe the sample preparation technique and their characterisation. In § 3 and § 4 we present respectively UPS and CVV Auger spectra obtained for Ni and Pd aggregates. The latter are interpreted theoretically in § 5 in the framework of the model presented in I.

## 2. Nucleation and growth of the aggregates

Since the experimental apparatus has been described elsewhere (Masson *et al* 1986, Hadj Romdhane *et al* 1989) we will limit ourselves here to a description of the preparation of the samples. They are prepared under high vacuum conditions ( $10^{-9}$  Torr) by vapour deposition of pure Ni and Pd (99.999%) on a flat amorphous silica substrate (200 Å thick) obtained by thermal oxidation of a silicon single crystal. The studied element is deposited at room temperature (at a rate from  $10^{13}$  to  $5 \times 10^{13}$  atoms  $\text{cm}^{-2} \text{s}^{-1}$ ), using a particular Knudsen cell (Bellamy and Colomer 1984) as the evaporation source. The atomic flux delivered by this Knudsen cell was calibrated with Rutherford backscattering measurements.

Thermodynamic arguments indicate that the growth mechanism of Ni and Pd, when their vapours are condensed onto an insulating substrate, follows a Volmer–Weber model, i.e. it is characterised by a distribution of 3D nuclei (Masson 1986). In this model, the process of island growth may be described as follows: the Pd atoms arriving on the substrate will be accommodated instantaneously, but the mean time  $\tau_s$  that such a single atom remains on the substrate before re-evaporation, is given by

$$\tau_s = \tau_0 \exp(E_a/kT)$$

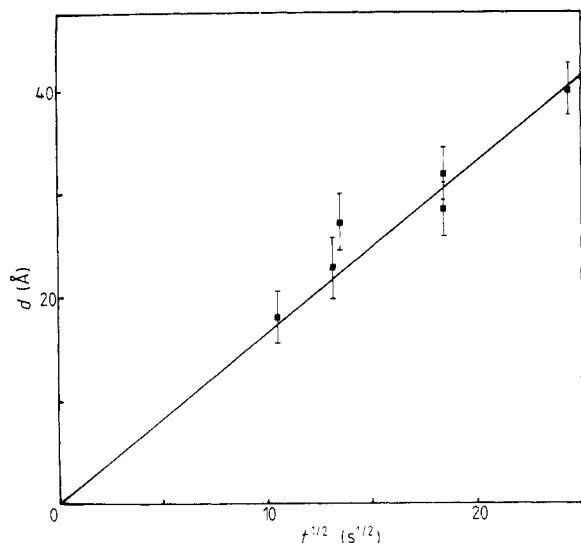
where  $\tau$  is a characteristic time related to the vibrational spectrum of the substrate and is of the order of the inverse Debye frequency,  $E_a$  is the adsorption energy and  $T$  the temperature. In general, the activation energy for diffusion  $E_d$  is smaller than  $E_a$ . Therefore, the single atom will move over the surface with a characteristic time  $\tau_d < \tau_s$ . Thus, it is after a random walk that an atom sticks to a cluster already present. When the nucleus density at saturation  $N_s$  is reached, the variation of the particle size  $d$  is given by (Schmeisser 1974)

$$d \propto 2(R \exp[(E_a - E_d)/2kT])^{1/2} t^{1/2} \quad (1)$$

where  $R$  is the impinging flux of atoms and  $t$  the evaporation time. The nucleus density at saturation  $N_s$  and the mean size of particles  $d$  have been determined by electron microscopy. We have found:  $N_s = (3.2 \pm 0.5) \times 10^{12}$  nuclei  $\text{cm}^{-2}$  with an impinging atom flux  $R = 10^{13}$  atoms  $\text{cm}^{-2} \text{s}^{-1}$ . We have performed several evaporations with a constant atomic flux  $R$  for different times  $t$ . Figure 1 represents the variation of mean diameters versus the square root of time: the straight line obtained is in agreement with (1).

## 3. Ultraviolet photoelectron spectra

The UPS experiments have been performed using He(I) as a UV source. The corresponding Ni and Pd valence bands as a function of the particle size are shown in figures



**Figure 1.** Variation of the mean diameter of palladium clusters deposited on silica substrate versus the square root of evaporation time. Impinging flux  $R = (3.0 \pm 0.5) \times 10^{12}$  atoms  $\text{cm}^{-2} \text{s}^{-1}$ .

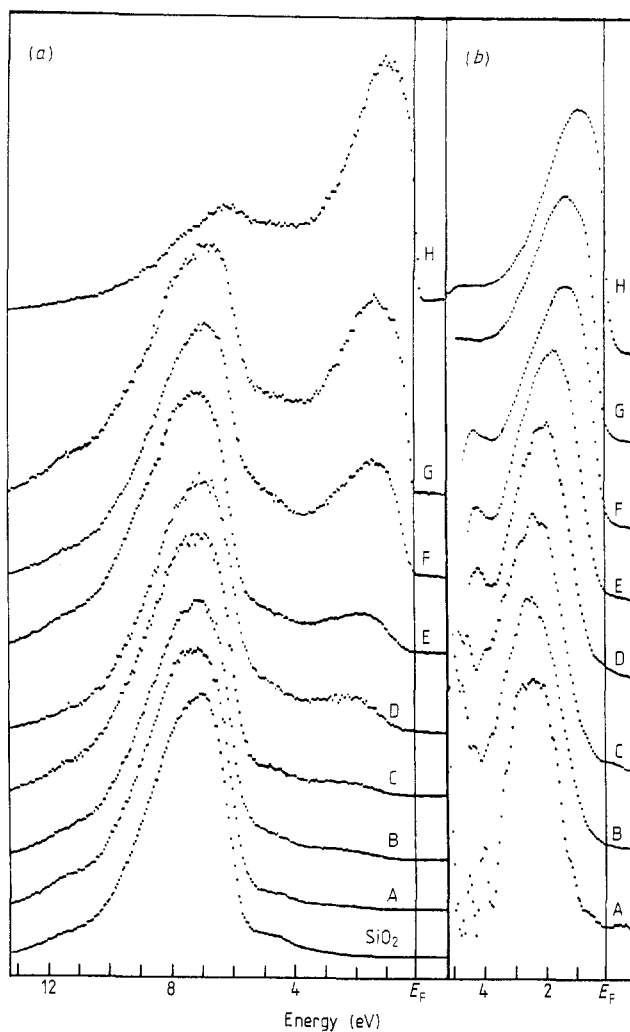
2(a) and 3(a) respectively. In figures 2(b) and 3(b) we have represented the difference spectra obtained by subtraction of the silica valence band with a softening factor corresponding to the loss of intensity linked to the absolute coverage of Ni or Pd on the surface. This softening factor is calculated as the ratio of the maximum intensity of the silica valence band in the (Ni or Pd)-SiO<sub>2</sub> systems against its intensity in the clean silica.

In both cases, we have observed a decrease of the FWHM of the valence bands when the particle size decreases: the narrowing between the highest and lowest coverages is  $0.76 \pm 0.13$  eV for Ni and  $1.1 \pm 0.13$  eV for Pd. The FWHM determined for the highest coverage ( $2.5 \pm 0.13$  eV for Ni and  $3.6 \pm 0.13$  eV for Pd) are in good agreement with those measured by Fuggle *et al* (1983) on a bulk sample (2.4 eV for Ni and 4.1 eV for Pd). Actually, this slight discrepancy between our measured FWHM for Pd and that obtained by Fuggle *et al* (1983) can be explained by the fact that in our case the Pd clusters are not large enough to exhibit the properties of the bulk. Indeed the total coverage for Pd is  $9 \times 10^{15}$  atoms  $\text{cm}^{-2}$  while for Ni, which presents the bulk properties, it is  $1.9 \times 10^{16}$  atoms  $\text{cm}^{-2}$ .

This phenomenon has been observed in all photo-emission studies of supported metal clusters (Liang *et al* 1976, Mason and Baetzold 1976, Mason *et al* 1977, Egelhoff and Tibbets 1979, Takasu *et al* 1978, Roulet *et al* 1980, Wertheim *et al* 1983, Kohiki and Ikeda 1986). This is expected on the basis of decreasing coordination numbers, since the mean d-bandwidth in a tight-binding approximation is proportional to the square root of the number of nearest neighbours (Haydock and Kelly 1973, Desjonquères and Cyrot-Lackmann 1975):

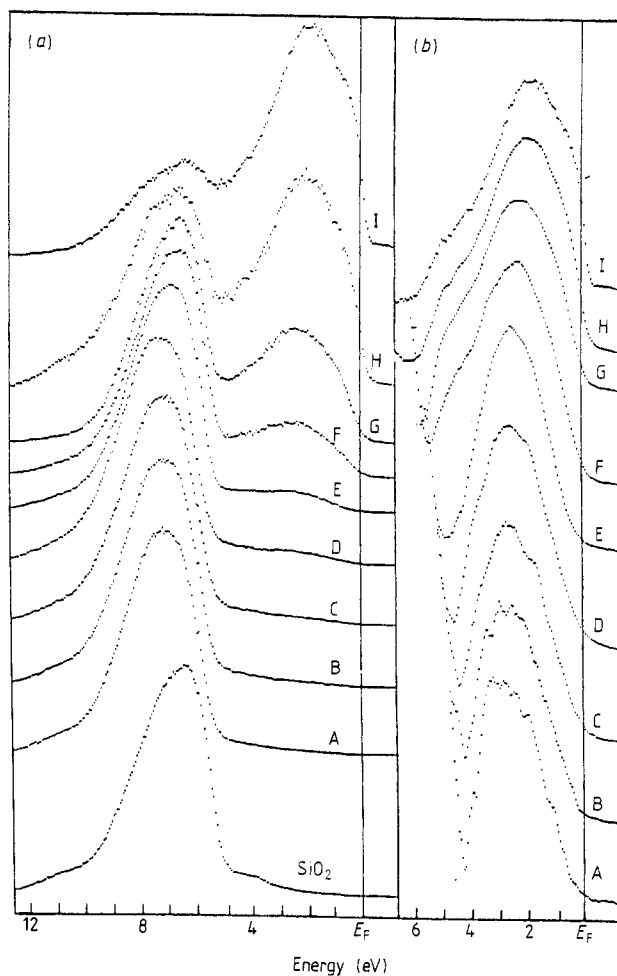
$$W \propto \beta Z^{1/2} \quad (2)$$

where  $\beta$  is an effective hopping integral and  $Z$  is the average coordination number which decreases as the particle size decreases. This effect can be calculated by assuming cubooctahedral clusters. Within this assumption, the smallest Pd cluster used in experiments ( $d \sim 5$  Å) corresponds to  $Z \approx 5.5$  while in the bulk  $Z = 12$ . According to (2) the resulting variation of the FWHM is a broadening which should not exceed  $\sim 30\%$  which is in good agreement with the experimental observations. For Ni the clusters at the beginning of



**Figure 2.** (a) He I photo-electron spectra of the valence band of Ni particles for different coverages on a silica substrate. Coverages in  $10^{15}$  atoms  $\text{cm}^{-2}$ : curve A, 0.48; curve B, 0.92; curve C, 1.5; curve D, 1.9; curve E, 5.6; curve F, 7.1; curve G, 13.2; curve H, 19. (b) As (a), but with the contribution of the silica substrate subtracted. Note that in all spectra the energies are referred to the Fermi level of bulk Ni.

the growth being larger ( $d \sim 20 \text{ \AA}$ ), the calculated variation of FWHM should be smaller (13%) while the experimental one is  $\sim 30\%$ . This discrepancy may be due to electron correlation effects. Actually, it is known (Tréglia *et al* 1982) that electron correlation effects reduce the apparent d-bandwidth, this narrowing being roughly proportional to  $(U^2/W)n_h(1 - n_h)$  where  $U$  is the Coulomb interaction,  $W$  the d-bandwidth and  $n_h$  the number of d holes per spin orbital. When the cluster size increases,  $U/W$  decreases so that the narrowing due to correlation effects becomes less important. As a result, this effect will reinforce the broadening with increasing size for both metals. This is indeed observed in Ni but not in Pd. This can be understood by a variation of  $n_h$  which increases when going from the atom to the solid in Pd and decreases in Ni, as will be discussed in



**Figure 3.** (a) He I photo-electron spectra of the valence band of Pd particles for different coverages on a silica substrate. Coverages in  $10^{14}$  atoms  $\text{cm}^{-2}$ : curve A, 0.14; curve B, 0.82; curve C, 1.6; curve D, 3.3; curve E, 8; curve F, 16; curve G, 33; curve H, 54; curve I, 98. (b) As (a), but with the contribution of the silica substrate subtracted. Note that in all spectra the energies are referred to the Fermi level of bulk Pd.

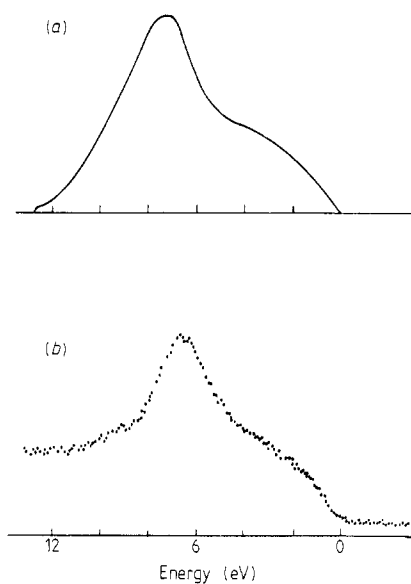
the following section and therefore correlation effects, when compared to the bulk case, are enhanced in small clusters of Ni and reduced in small clusters of Pd.

#### 4. CVV Auger spectra

Now, we present and discuss the results obtained by Auger electron spectroscopy on the same samples, studying the LVV ( $L_3M_{4,5}M_{4,5}$ ) spectra of nickel and MVV ( $M_{4,5}N_{4,5}N_{4,5}$ ) spectra of palladium. In the one-electron approximation, the kinetic energy  $E_k$  of the outgoing Auger electron can be written

$$E_k = E_c - E_{v1} - E_{v2} \quad (3)$$

where  $E_c$ ,  $E_{v1}$ ,  $E_{v2}$  are respectively the binding energies of the core and the two valence

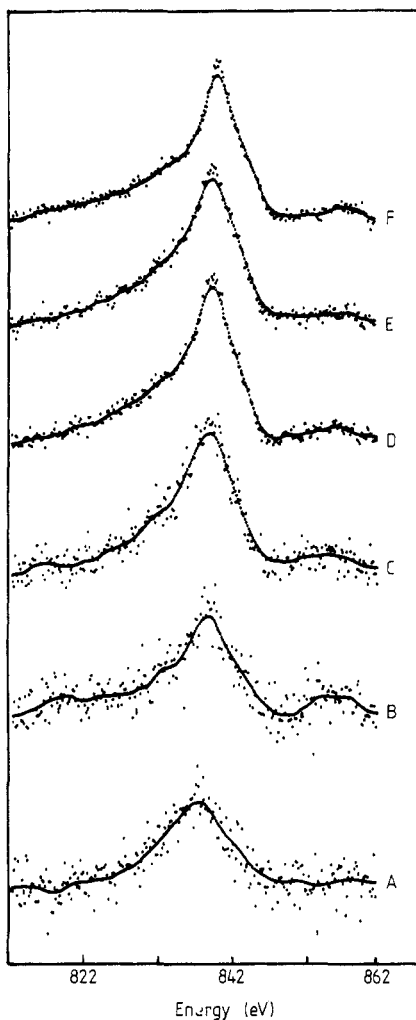


**Figure 4.** Comparison between (a) the two-hole spectrum calculated in I for Ni ( $U = 2$  eV) and (b) the experimental spectrum obtained by Bennett *et al* (1983).

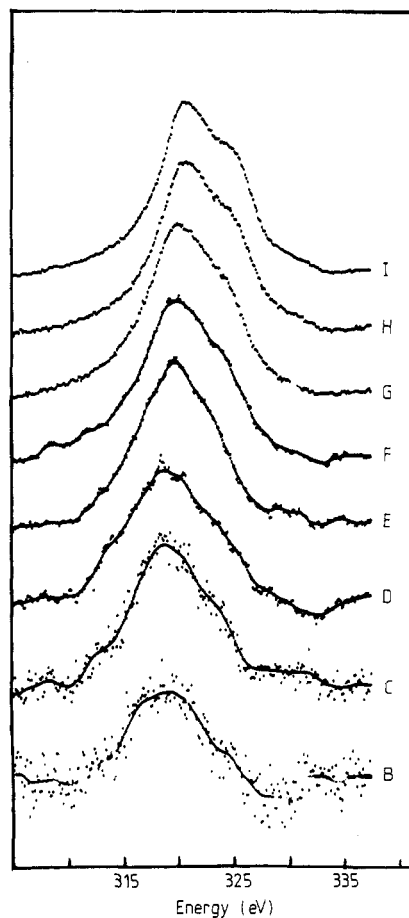
electrons. Therefore, if we assume a constant transition matrix element along the valence band, the Auger spectrum is given by the self-convolution of the valence density-of-states. If we now take electron correlations into account in the strong-correlation limit ( $U \gg W$ ), (3) becomes

$$E_k = E_c - E_{v1} - E_{v2} - U. \quad (4)$$

Using a  $t$ -matrix approximation Cini (1977, 1978, 1979) and Sawatzky (1977) have shown that the Auger spectrum has a quasi-atomic character when the ratio  $U/W$  is large enough, due to the presence of a localised two-hole bound state. This model was used by Yin *et al* (1977) and Antonides *et al* (1977) to derive the values of  $U$  from the experimental spectra of Fe, Co and Ni. However, these values were not in agreement with those deduced from the experimental band structure determined by angle resolved photo-emission experiments (Tréglia *et al* 1982). This is not very surprising since the  $t$ -matrix approximation is only valid for filled bands, which is not the case for Fe, Co or Ni. It was thus necessary to generalise the theory of Cini and Sawatzky to an arbitrary number of d holes. This has been done in I, where it was shown that the Auger lineshape is drastically modified as a function of the number of d holes for a nearly filled band. Let us emphasise that in the calculations in I, the influence of the final state multiplet structure on the Auger profile was not considered. Actually, such a structure arises from the coupling between the two final state holes in the atomic limit ( $U/W \gg 1$ ). In the band limit ( $U = 0$ ), the two holes are completely delocalised and the multiplet structure disappears. In the case of Pd and Ni, we have  $0.3 < U/W < 0.5$  and the band limit is better suited than the atomic one. This is confirmed by the excellent agreement they obtained between the calculated and experimental Auger spectra for Ni (see figure 4) without any adjustable parameter. Indeed the only input parameter  $U$  has been taken from photo-emission experiments on the valence bands (Tréglia *et al* 1982). Therefore, one can hope to get information on the variation of the number of holes in the d band as a function of the aggregate size from the corresponding variation of the FWHM of the Auger spectrum. In this respect the comparative study of Ni and Pd aggregates is



**Figure 5.** LVV Ni Auger spectra for different coverages of Ni on SiO<sub>2</sub>. Coverages in 10<sup>15</sup> atoms cm<sup>-2</sup>: curve A, 0.92; curve B, 1.5; curve C, 1.9; curve D, 5.6; curve E, 7.1; curve F, 19. The kinetic energies of the Auger electrons are given in eV.

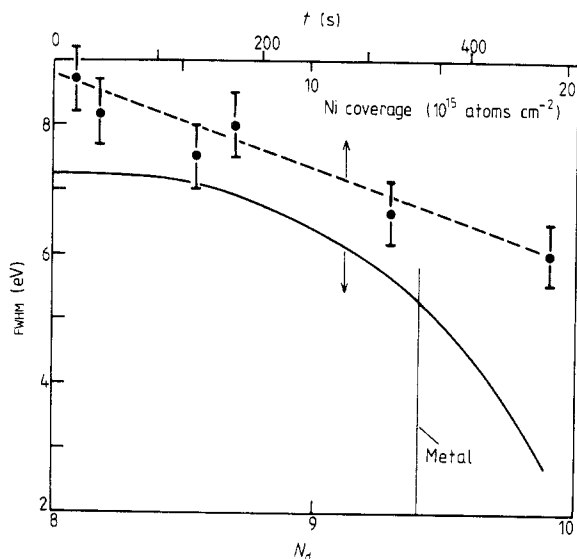


**Figure 6.** MVV Pd Auger spectra for different coverages of Pd on SiO<sub>2</sub>. Coverages in 10<sup>14</sup> atoms cm<sup>-2</sup>: curve B, 0.82; curve C, 1.6; curve D, 3.3; curve E, 8; curve F, 16; curve G, 33; curve H, 54; curve I, 98. The kinetic energies of the Auger electrons are given in eV.

particularly interesting since the number of valence d holes varies in opposite directions when going from the atom to the solid. Indeed the electronic configuration is 3d<sup>8</sup>4s<sup>2</sup> for Ni and 4d<sup>10</sup>5s<sup>0</sup> for Pd in the free atom state, whereas it becomes 3d<sup>9.4</sup>4s<sup>0.6</sup> for Ni and 4d<sup>9.64</sup>5s<sup>0.36</sup> for Pd in the bulk state.

In figures 5 and 6 we show the LVV (Ni) and MVV (Pd) Auger spectra for the different coverages, or equivalently, for different sizes. These spectra have been corrected for the background, i.e. for inelastic scattering either by the subtraction of the background with a multiple linear regression (Bevington 1969) or by the subtraction of the substrate Auger signal corresponding to the same energy range. The results obtained in both cases are similar; however in the latter we obtain noisier spectra.





**Figure 7.** Experimental (broken curve) and theoretical (full curve) variations of the FWHM of LVV Ni Auger spectra as a function of the nickel coverage and evaporation time (experiment: upper scale) and the number of d electrons  $N_d$  (theory with  $U/W = 0.5$ : lower scale).

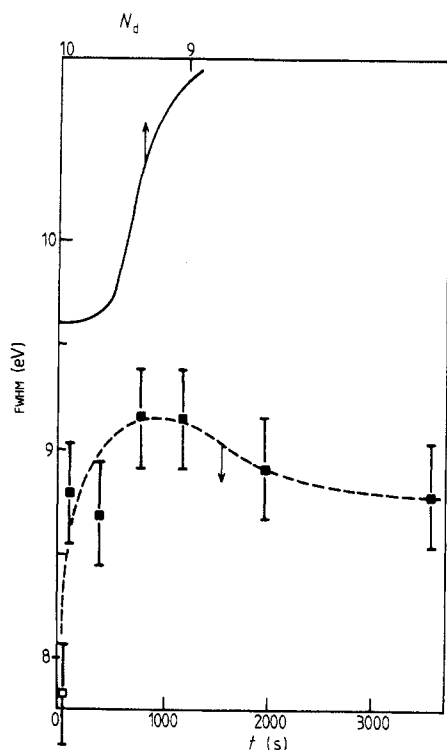
We note on these figures, first a sizable shift of 3.5 eV for the Ni LVV transition and 2.4 eV for the Pd MVV transition between the bulk and the smallest clusters, then, a variation of the Auger lineshape with the cluster size. The energy shift might be due to the variation of the Fermi level, to the modification of the core-level binding energy due to the shift of the initial core state energy and to the extra-atomic relaxation energy (Bellamy 1987) which is of the order of a few eV between the free atom and the solid (Johansson and Mårtensson 1980). We will not discuss this point further here and will focus now on the second point. In the case of Ni (see figure 7) the FWHM of the Auger line continuously decreases from 8.8 eV to 6 eV when the cluster size increases whereas, in the case of Pd, it increases and reaches a maximum for crystallite sizes of 25–35 Å and then slightly decreases as can be seen in figure 8.

## 5. Theoretical interpretation

Three mechanisms lead to a variation with size of the FWHM of the Auger spectra:

(i) the broadening of the local density of states with the increasing size of the crystallites due to the variation of their average coordination number  $Z$ , which has been discussed above. Even though it could explain qualitatively the variation of the FWHM in the earliest stages of Pd cluster growth, it cannot account for the different behaviours of Ni and Pd.

(ii) the inhomogeneous broadening induced by the variation of the core-electron binding energy as a function of the geometrical environment of the excited atoms in the cluster. At the kinetic energies of the experiment, the mean free path of the Auger electron is such that all the atoms in the cluster contribute a similar amount to the total emission. Thus, when the crystallite size increases, the ratio of the number of surface sites to that of the bulk sites decreases leading finally to a negligible inhomogeneous broadening for very large clusters. Here, this ratio can be estimated for the cubo-octahedral geometry: it varies from 1 (half of the surface atoms being edge atoms) for



**Figure 8.** Experimental (broken curve) and theoretical (full curve) variations of the FWHM of MVV Pd Auger spectra as a function of evaporation time (experiment: lower scale) and the number of d electrons  $N_d$  (theory with  $U/W = 0.3$ : upper scale).

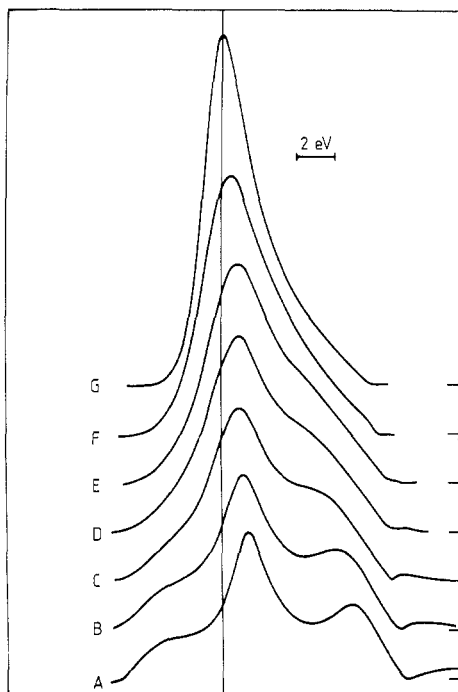
particles with a diameter of  $\sim 20$  Å to  $0.5$  (30% of the surface atoms being edge atoms) for particles with a diameter of  $\sim 35$  Å. The usual surface core-level shifts being of the order of a few  $0.1$  eV (for a review see Guillot 1985, Spanjaard *et al* 1985, Desjonquères *et al* 1987, Tréglia *et al* 1988), the broadening should be smaller than this value.

(iii) the electronic correlation effects discussed above. Their estimation for a fixed bandwidth needs the knowledge of two parameters: the number of d holes  $n_h$  and the Coulomb integral  $U$ . As discussed in I, an increase of  $n_h$  from zero broadens the Auger line, the more as  $U$  is large. We have thus calculated the Auger spectra of Ni and Pd as a function of the number of d holes for realistic and constant values of  $U$ .

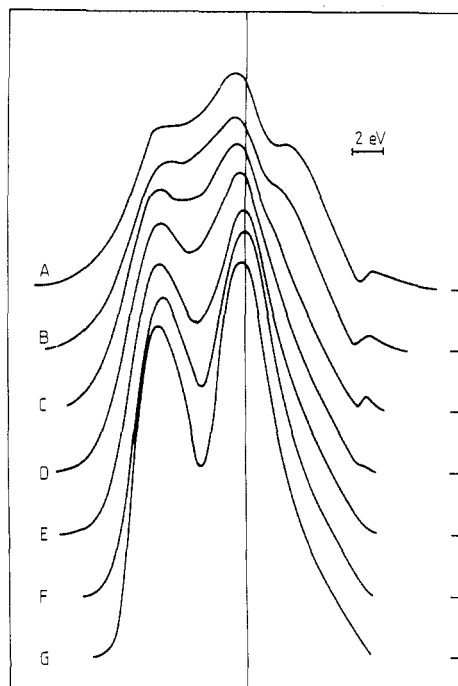
Let us first present our results for Ni. In this case, the energy of the  $L_3$  core electron involved in the Auger process is far enough from the energies of the  $L_2$  and  $L_1$  levels to allow us to consider only one level.

As shown in I we can replace the exact density of states by a rectangular one, with the same second moment. The ratio  $U/W = 0.5$  is derived from photo-emission data (Tréglia *et al* 1982). The calculated spectra are shown in figure 9 for  $n_h$  varying from  $0.2$  (free atom) to  $0.02$  (metal  $0.06$ ). The overall agreement with the experimental spectra of figure 5 is highly satisfactory. The theoretical FWHM of these Auger peaks are compared with experiments in figure 7. The evolution of the width as a function of the particle size is very well reproduced. The slight difference in absolute value can be attributed to the instrumental resolution, the inhomogeneous broadening . . .

The case of Pd is more intricate since in the energy range studied two core levels are involved ( $M_4$ ,  $M_5$ ), separated by  $\sim 5.8$  eV (Herman and Skillman 1963), so that the corresponding Auger peaks cannot be resolved due to their widths. We have thus



**Figure 9.** Theoretical LVV Ni Auger spectra as a function of the number of d electrons for  $U/W = 0.5$ . Curve A,  $N_d = 8$ ; curve B,  $N_d = 8.5$ ; curve C,  $N_d = 9$ ; curve D,  $N_d = 9.2$ ; curve E,  $N_d = 9.4$ ; curve F,  $N_d = 9.6$ ; curve G,  $N_d = 9.8$ .



**Figure 10.** Theoretical  $M_{4,5}VV$  Pd Auger spectra as a function of the number of d holes for  $U/W = 0.3$ . Curves labelled as in figure 9, illustrating the opposite trend in the two aggregates.

superimposed the two corresponding theoretical Auger spectra, assuming equal intensities. The results are given in figure 10 for  $N_d$  varying from 0.02 (free atom: 0) to 0.2 (metal: 0.36) and for a realistic value of  $U/W$  (0.3). A comparison of the evolution of experimental (figure 6) and theoretical (figure 10) spectra as a function of size is gratifying. Let us note, however, that the two Auger lines are better resolved in the theoretical spectra than in the experimental ones at low coverage. This discrepancy should disappear by allowing an increase of  $U/W$  when going from the metal to a very small cluster. Actually, as is seen experimentally,  $W$  decreases and  $U$  is expected to increase in this process, due to a less efficient screening. Moreover the respective intensity of the two main peaks should be improved if, instead of assuming equal intensities for the two components, one uses a more realistic ratio (McGuire 1972). The corresponding FWHM is compared with experiment in figure 8. The increasing part of the curve is satisfactorily reproduced. The slight decrease of FWHM for particles larger than 25 Å can be explained by the inhomogeneous broadening and the decrease of  $U$  with increasing size of the cluster if we assume that the bulk configuration is almost reached for 25–35 Å particles.

Let us finally mention that particle size distribution could also lead to an additional broadening of the Auger lineshape.

## 6. Conclusion

We have presented here an experimental investigation of the UPS and Auger spectra of Ni and Pd aggregates on a  $\text{SiO}_2$  substrate which shows surprising results. Whereas the

width of the UPS spectra increases for both metals when the crystallite size increases, the width of their Auger spectra increases for Pd and decreases for Ni. These results can be interpreted theoretically by a continuous change of the electronic configuration from the free atom to the bulk. However, as discussed above, the variation of the valence bandwidth with size should also be taken into account. Therefore, it would be highly desirable to perform calculations that include this variation of bandwidth and correlation effects simultaneously. Such a calculation can easily be performed but is only meaningful if the geometry of the clusters at the earliest stage of growth is better known. In this respect, information drawn from scanning tunnelling microscopy experiments should be very interesting.

## References

- Antonides E, Janse E C and Sawatzky G A 1977 *Phys. Rev. B* **15** 1669  
Bellamy B and Colomer G 1984 *J. Vac. Sci. Technol. A* **2** 1604  
Bellamy B 1987 *PhD Thesis* Université de Paris  
Bennett P A, Fuggle J C, Hillebrecht F U, Lenselink A and Sawatzky G A 1983 *Phys. Rev. B* **27** 2194  
Bevington P R 1969 *Data Reduction and Error Analysis for the Physical Sciences* (New York: McGraw-Hill) p 164  
Cini M 1977 *Solid State Commun.* **24** 681  
— 1978 *Phys. Rev. B* **17** 2788  
— 1979 *Surf. Sci.* **87** 483  
Desjonquères M C and Cyrot-Lackmann F 1975 *Surf. Sci.* **53** 429  
Desjonquères M C, Sébilleau D, Tréglia G, Spanjaard D, Guillot C, Chauveau D and Lecante J 1987 *Scan. Microsc.* **1** 1557  
Egelhoff W F and Tibbets G G 1979 *Phys. Rev. B* **19** 5028  
Fuggle J C, Hillebrecht F U, Zeller R, Bennet P and Freiburg Ch 1983 *Phys. Rev. B* **27** 2145  
Guillot C 1985 *PhD Thesis* Université de Paris  
Hadj Romdhane Y, Bellamy B, De Gouveia V, Masson A and Che M 1989 *Appl. Surf. Sci.* at press  
Haydock R and Kelly M J 1973 *Surf. Sci.* **38** 139  
Herman F and Skillman S 1963 *Atomic Structure Calculations* (Englewoods Cliffs, NJ: Prentice Hall)  
Johansson B and Mårtensson N 1980 *Phys. Rev. B* **21** 4427  
Kohiki S and Ikeda S 1986 *Phys. Rev. B* **34** 3786  
Liang K S, Salaneck W R and Aksay I A 1976 *Solid State Commun.* **19** 329  
Mason M G and Baetzold R C 1976 *J. Chem. Phys.* **64** 271  
Mason M G, Gerenser L J and Lee S T 1977 *Phys. Rev. Lett.* **39** 288  
Masson A, Bellamy B, Hadj Romdhane Y, Che M, Roulet H and Dufour G 1986 *Surf. Sci.* **173** 479  
Masson A 1986 *Contribution of Clusters Physics to Material Science and Technology* ed. J Davenas and P Rabette (NATO ASI Series, E vol 104) (Dordrecht: Nijhoff) p 295  
McGuire E J 1972 *Phys. Rev. A* **5** 1043  
Roulet H, Mariot J M, Dufour G and Hague C F 1980 *J. Phys. F: Met. Phys.* **10** 1025  
Sawatzky G A 1977 *Phys. Rev. Lett.* **39** 504  
Schmeisser H 1974 *Thin Solid Films* **22** 83  
Spanjaard D, Guillot C, Desjonquères M C, Tréglia G and Lecante J 1985 *Surf. Sci. Rep.* **5** 1  
Takasu Y, Unwin R, Tesche B, Bradshaw A M and Grunze M 1978 *Surf. Sci.* **77** 219  
Tréglia G, Desjonquères M C, Ducastelle F and Spanjaard D 1981 *J. Phys. C: Solid State Phys.* **14** 4347  
Tréglia G, Ducastelle F and Spanjaard D 1982 *J. Physique* **43** 341  
Tréglia G, Sébilleau D, Desjonquères M C, Spanjaard D, Guillot C, Chauveau D and Lecante J 1988 *Springer Series in Solid State Sciences* vol 81 (Berlin: Springer) p 281  
Wertheim G K, DiCenzo S B and Youngquist S E 1983 *Phys. Rev. Lett.* **51** 2310  
Yin L, Tsang T and Adler I 1977 *Phys. Rev. B* **15** 2974