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# Determination of the particle size required for bulk metallic properties

R. C. Baetzold, M. G. Mason, and J. F. Hamilton

Research Laboratories, Eastman Kodak Company, Rochester, New York 14650

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Small transition-metal clusters have been prepared by vacuum deposition and characterized by transmission electron microscopy. The valence bandwidth has been measured by x-ray photoelectron spectroscopy (XPS) and compared with the theoretical prediction of extended Hückel and self-consistent-field  $X\alpha$  scattered-wave molecular-orbital calculations. The semiempirical extended Hückel calculations agree much better with the experimentally determined values.

## INTRODUCTION

Considerable controversy surrounds the determination of the number of atoms required for a metallic cluster to exhibit properties characteristic of the bulk metal.<sup>1,2</sup> Recently there has been a growing recognition that such a question is much too general. At best, one can only hope to determine the required size for a cluster of a given composition to exhibit a specific bulk property. Even within this highly restrictive sense the answer may be open to interpretation, as many properties such as the ionization potential and electron affinity are thought to converge slowly to the bulk values.<sup>2</sup> Nevertheless, other properties such as valence bandwidth are expected to converge more rapidly and have been used in several theoretical studies as a criterion for bulklike electronic structure.<sup>1-3</sup>

The two most common theoretical approaches for calculating the electronic structure of metal clusters are the self-consistent-field  $X\alpha$  scattered-wave (SCF- $X\alpha$ -SW) method<sup>1</sup> and the semiempirical molecular-orbital methods such as extended Hückel (EH) and complete neglect of differential overlap (CNDO).<sup>2</sup> These two formalisms differ dramatically in their predictions of the bandwidth dependence on transition- and noble-metal cluster size. The SCF- $X\alpha$ -SW method as employed by Messmer *et al.* predicts that "the electronic structures of small clusters ( $\geq 10$  atoms) and the bulk metal are not fundamentally different"<sup>3</sup> and that clusters with 8-13 atoms show many bulk features. Other calculations with this method have employed small clusters (6 atoms) to treat chemisorption and found agreement between such small models and experimental UPS spectra of the bulk.<sup>4</sup> Yet if the bulk DOS is attained for a few atoms with the SCF- $X\alpha$ -SW calculation, it is unclear why the local density of states is so different for bulk and surface atoms as in the  $Ni_{13}$  cluster of Ref. 1. In addition, Mitchell and co-workers<sup>5</sup> using this method have calculated a bandwidth of only 0.35 eV for the central atom in a  $Ag_{19}$  cluster relative to the bulk value of 3.2 eV. Bulklike features would be expected if these properties had converged with size.

Contrary to the SCF- $X\alpha$ -SW results are the semiempirical EH calculations, which indicate much larger clusters are required to attain bulk properties. The  $d$  bandwidth of 39-atom silver clusters is less than 80% of that calculated for the bulk by the same method.<sup>2</sup> In addition, ionization potential, binding energy, and

energy gap values<sup>6</sup> which differ significantly from the bulk value have been calculated by EH for 55-atom silver clusters. This communication compares the results of these two theoretical approaches with the widths of supported metal clusters as measured by x-ray photoelectron spectroscopy (XPS).

Details of sample preparation techniques and photoemission measurements have been reported.<sup>7</sup> The samples are prepared by vapor deposition onto amorphous carbon substrates. The particle size distributions are determined by electron microscopy. Electron diffraction patterns can be recorded from deposits down to a minimum coverage of slightly over  $1 \times 10^{15}$  atoms/cm<sup>2</sup>. Only the metallic phase can be detected. The XPS spectra are recorded on a Hewlett-Packard 5950A ESCA spectrometer. The instrumental contribution to the measured line widths is  $\sim 0.6$  eV.

The measured full widths at half maximum (FWHM) as a function of coverage for Pd, Pt, Rh, and Ir are shown in Fig. 1. In all four metals the bulk width is not achieved until coverages of  $> 2 \times 10^{15}$  atoms/cm<sup>2</sup> are reached. Transmission electron micrographs show that the average particle size at this coverage is  $\sim 15$  Å. Assuming hemispherical shapes<sup>8</sup> and bond distances appropriate for the bulk metals, the number of atoms per cluster is  $\sim 400$ . Figure 2 is a transmission electron micrograph of Pt clusters at a nonbulklike coverage of  $2 \times 10^{15}$  atoms/cm<sup>2</sup>. An error of two in the coverage necessary to reach the bulk FWHM would cause an error of  $< 3$  in the average number of atoms per cluster.<sup>7</sup> An error of more than an order of magnitude,

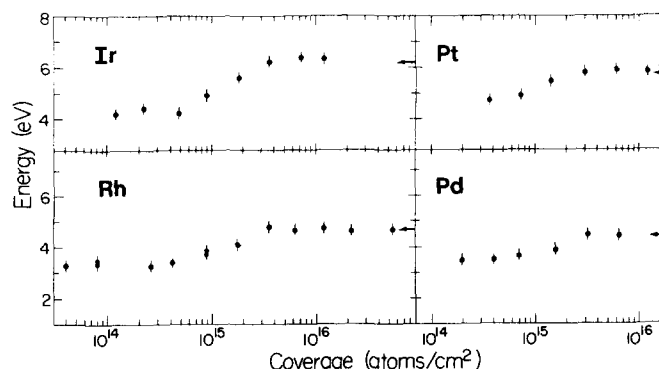


FIG. 1. Variation in the measured valence bandwidth (full width at half maximum) as a function of deposited metal.

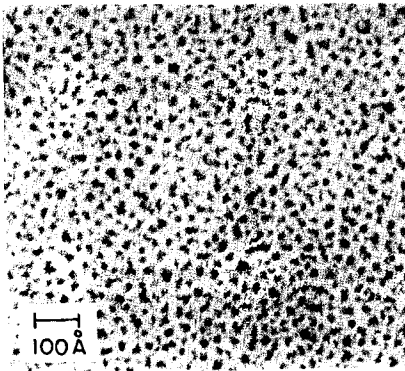


FIG. 2. Transmission electron micrograph of Pt cluster on carbon at a coverage of  $2 \times 10^{15}$  atoms/cm<sup>2</sup>.

which would be required to make these results consistent with the SCF- $X\alpha$ -SW predictions, seems highly unlikely.

In interpreting these results, two cautions should be considered. First, the clusters are not monodispersed but are characterized by a size distribution related to the Poisson function.<sup>7</sup> Second, the metal clusters are not isolated but are supported on a potentially interactive substrate.

In terms of the experimentally determined FWHM, it seems most reasonable that these factors would result in artificial line broadening rather than line narrowing as would be required for agreement with the SCF- $X\alpha$ -SW calculations. In conclusion, the experimentally measured FWHM of the valence orbitals of Pd, Pt, Rh, and Ir clusters disagree with the predictions of the SCF- $X\alpha$ -SW calculation.

Extended Hückel calculations of the density of states for large palladium clusters and bulk were performed for comparison with these experiments. Clusters having the face-centered-cubic geometry were examined. Each atom contains 4*d*, 5*s*, and 5*p* atomic Slater orbit-

TABLE I. Parameters of the calculation.

Orbital	Exponent	$-H_{ii}$ (eV)
5 <i>p</i>	2.190	1.84
5 <i>s</i>	1.568	7.69
4 <i>d</i>	5.9830 (0.5264) <sup>a</sup>	10.99
	2.613 (0.6372)	

<sup>a</sup>Double Slater orbitals with the exponents and coefficients in parentheses were employed.

als in the fashion of a standard EH calculation with the parameters given in Table I. Spherical clusters having complete shells of neighbors are those with 13, 19, 43, 55, and 79 atoms. The density of states plots in Fig. 3 are prepared by summing the set of Gaussian functions with 0.1 eV FWHM which are centered upon each energy level. The summation is then normalized. Details of the bulk calculation have been reported<sup>2</sup> and employ the same parameters and approximations as the cluster calculation.

The detailed calculated densities of states for palladium clusters and bulk are shown in Fig. 3. Here the buildup of the *d* band is shown for the spherical clusters to take place up to a cluster size of 79 atoms, which has a *d* bandwidth 86% of that calculated for the bulk. The smaller clusters have narrower bandwidths, and at 13 atoms only 50% of the *d* bandwidth is present. This type of behavior is also observed for other metal clusters, such as Cu and Rh, and is a fundamental characteristic of the EH method. The result is not parameter dependent, since identical parameters and approximations are employed for the cluster and bulk calculation. The behavior of clusters having incomplete shells of atoms also deserves note. The shape of the DOS of these clusters (31 and 67 atoms) deviates significantly from the corresponding DOS for symmetric clusters. This feature is consistent with a large cluster size re-

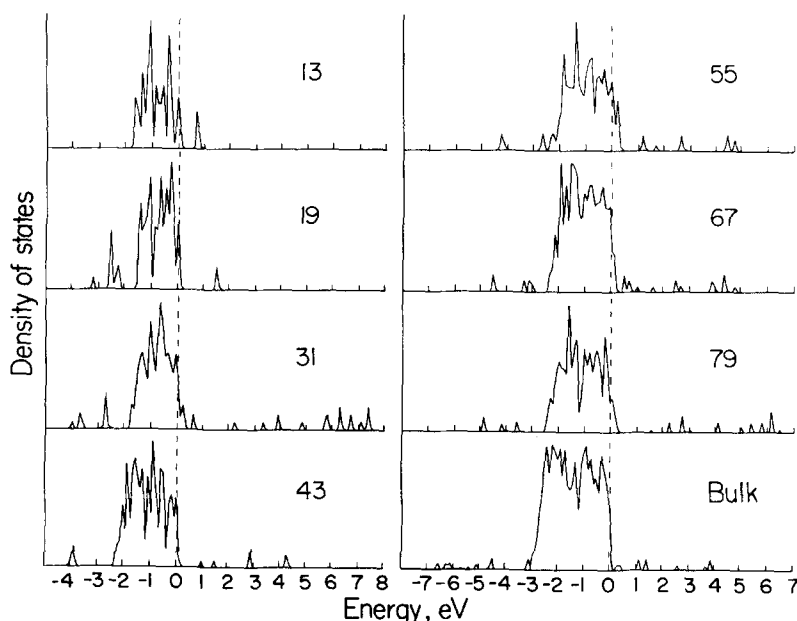


FIG. 3. Calculated densities of states for Pd clusters at various particle sizes. Line-widths have been broadened by a 0.1 eV Gaussian function.

quired for convergence. We tabulate the  $d$  bandwidths calculated for various clusters using the noniterative EH approach below. These results show the degree of  $d$  band broadening with size.

cluster	Pd <sub>2</sub>	Pd <sub>13</sub>	Pd <sub>19</sub>	Pd <sub>31</sub>	Pd <sub>43</sub>	Pd <sub>55</sub>	Pd <sub>67</sub>	Pd <sub>79</sub>	Bulk
$d$ bandwidth (eV)	0.80	1.54	2.04	2.26	2.42	2.57	2.55	2.65	3.08

We have compared the results of two calculating procedures with experiment to determine which one more accurately reproduces cluster properties. The popular SCF- $X\alpha$ -SW method predicts bulk properties at too small a size, and the claims of Ref. 1 are not fulfilled. The method, however, does give good bulk characteristics when used with only a few atoms. Thus, although the SCF- $X\alpha$ -SW method does not correctly predict cluster behavior, it offers an economy of time in exploring bulk behavior. The simple EH method is in substantial agreement with experiment in predicting the size for bulk bandwidth. The results of our past and present calculation are in substantial agreement with other calculations using *ab initio* and effective potential methods. For example, Schaefer and co-workers<sup>8</sup> found roughly half the bulk binding energy for Be clusters using *ab initio* methods. Hermann and Bagus studied Li clusters with up to nine atoms using *ab initio* techniques and concluded they were not bulklike in this size range.<sup>9</sup> More recently, Melius, Upton, and Goddard employed an effective potential method to study Ni clusters with up to 87 atoms.<sup>10</sup> The  $s$  orbital density of states showed considerable changes with size indicating that at least the upper part of this size range must be reached for convergence to the bulk.

<sup>1</sup>R. P. Messmer, S. K. Knudson, K. H. Johnson, J. B. Diamond, and C. Y. Wang, Phys. Rev. B **13**, 1396 (1976).

<sup>2</sup>R. C. Baetzold, J. Chem. Phys. **68**, 555 (1978).

<sup>3</sup>R. P. Messmer in *Semiempirical Methods of Electronic Structure Calculation*, edited by G. A. Segal (Plenum, New York, 1977), Vol. 8, Chap. 6.

<sup>4</sup>N. Rosch and D. Menzel, Chem. Phys. **13**, 243 (1976).

<sup>5</sup>J. D. Head, K. A. R. Mitchell, and L. Noodleman, Surf. Sci. **69**, 714 (1977).

<sup>6</sup>R. C. Baetzold and R. E. Mack, J. Chem. Phys. **62**, 1513 (1975). This reference shows that the  $d$  bandwidth of metal clusters calculated with single-zeta orbitals is probably too

narrow, but with double-zeta orbitals wider bands are found (e.g., 1.8 eV, for Pd<sub>19</sub>).

<sup>7</sup>J. F. Hamilton and P. C. Logel, Thin Solid Films **23**, 89 (1974).

<sup>8</sup>C. W. Bauschlicher, D. H. Liskow, C. F. Bender, and H. F. Schaefer III, J. Chem. Phys. **62**, 4815 (1975); C. W. Bauschlicher, C. F. Bender, H. F. Schaefer III, and P. S. Bagus, Chem. Phys. **15**, 227 (1976); C. W. Bauschlicher, Jr., P. S. Bagus, and H. F. Schaefer III, IBM J. Res. Develop. **22**, 213 (1978).

<sup>9</sup>F. Hermann and P. S. Bagus, Phys. Rev. B **17**, 4082 (1978).

<sup>10</sup>C. F. Melius, T. H. Upton, and W. A. Goddard III, Solid State Commun. **28**, 501 (1978).