Structure of Copper Microclusters Isolated in Solid Argon

P. A. Montano,[a] G. K. Shenoy, and E. E. Alp
Materials Science and Technology Division, Argonne National Laboratory, Argonne, Illinois 60439

and

W. Schulze and J. Urban
Fritz Haber Institute der Max Planck Gesellschaft, D-1000 Berlin 33, West Germany

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Extended x-ray-absorption fine structure has been used in conjunction with the gas-aggregation technique to investigate the structure of copper microclusters (7 to 15 Å mean diameter). The crystallographic structure of the microclusters is consistent with an fcc lattice. A small contraction of the nearest-neighbor distance was measured as a function of cluster size.

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Determination of the structure of small metal clusters is of fundamental importance in many areas of solid state physics and chemistry, including nucleation, growth morphology, catalysis, and other surface phenomena.[1] The most significant questions regarding the structure of these microclusters are related to (1) the interatomic distance, and (2) the modification of the atomic arrangement as a function of cluster size, as the cluster size is reduced to the critical nucleation size. In this Letter, we will address these questions on the basis of the experimental evidence that we have obtained on copper microclusters, and present the usefulness of the extended x-ray-absorption fine-structure (EXAFS) technique in such investigations. We believe that this is the first of such approaches in the study of the growth morphology of metal clusters.

In the past, we have produced metal-atom microclusters with a narrow size distribution using the gas-aggregation technique.[2,3] In this technique, the metal atoms are evaporated from a Knudsen cell in an argon atmosphere. The metal clusters are formed in a region of sufficiently high supersaturation. The metal clusters are then transported by the gas stream through an aperture into a liquid-helium cryopump, where most of the gas is condensed. A collimated molecular beam passes through a second aperture on the axis of the cryopump and is codeposited with argon gas onto a high-purity aluminum substrate at 4.2 K.

In the present experiments, the typical metal dilution in the solid argon matrix was 0.1–0.2 at.% metal. The size of the metal-atom clusters can be selected by a change of the deposition condition, i.e., the size of the aperture between the Knudsen-cell region and the cryopump. As opposed to the simple evaporation technique, in the gas-aggregation technique, one can obtain a narrow size distribution of about ±5 Å for clusters in the range of 25–150 Å. By forming copper microclusters in an inert gas matrix held at 4.2 K, one can study the structure without the interference of a strongly interacting substrate, which was used in the earlier studies.[4,5]

In the present measurements we used the same monitoring techniques as described in Ref. 3. We detected the coagulation of Au, Ag, and Cu particles on the carbon substrate held at 298 K used for transmission electron microscopy; such coagulation was observed even at $\frac{1}{10}$ sec sampling time. For particles less than 15 Å in diameter a rapid oxidation of the Cu microclusters was observed when exposed to the atmosphere. Consequently, the cluster-size determination was carried out by means of time-of-flight mass spectroscopy. The measurements were performed off-line, maintaining identical conditions to those used in the EXAFS measurements. (A rough estimate of the average particle size can also be obtained from the EXAFS measurements and agrees with the mass-spectrometry results.)

The x-ray absorption spectra were measured with use of the synchrotron radiation at the Stanford Synchrotron Radiation Laboratory. Both absorption and fluorescence spectra were collected for various cluster

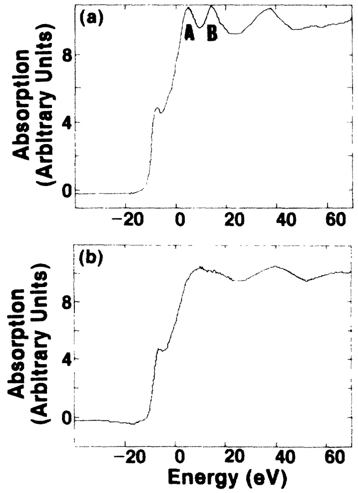

FIG. 1. XANES spectra for (a) Cu metal foil at room temperature and (b) 10-Å-mean-diameter particles in solid argon.

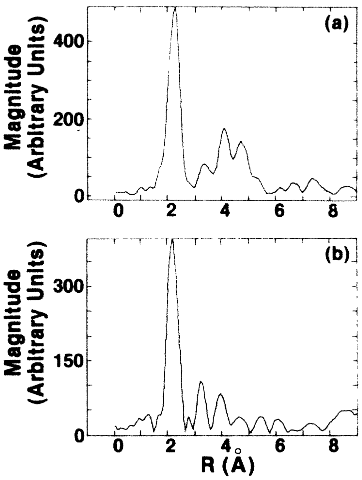

FIG. 2. Magnitude of the Fourier transforms of $k^3\chi(k)$ of (a) Cu metal foil and (b) 10-Å–mean-diameter particles.

sizes. At the dilute Cu concentrations used in the present studies, the agglomeration of clusters in the matrix did not occur. Figures 1(a) and 1(b) show the x-ray-absorption near-edge structure (XANES) for the metal foil and the 10-Å-diameter particles. The absence of two peaks, A and B, in the XANES of the microcluster, in contrast to the XANES of the bulk metal, indicates the absence of fourth- and higher-shell atoms in the cluster. Such XANES was observed in all samples investigated, from 15 Å to dimers. In addition, we have performed a computer simulation of the near-edge structure by excluding the fourth- and higher-shell contributions to the copper-metal spectrum, and found that the near-edge structure is very similar to those measured on the clusters. This is in very good agreement with the predictions of the multiple-scattering calculation.[6] The K-edge threshold for small clusters is found to be 1.4 eV higher than that of Cu metal.

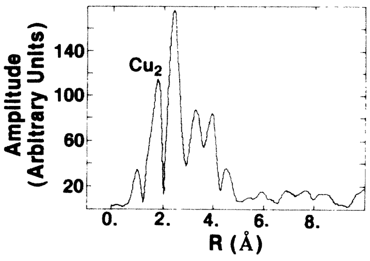

FIG. 3. Magnitude of the Fourier transform of $k^3\chi(k)$ for a sample containing Cu_2 and particles of 6–7 Å mean diameter.

Because of their higher statistical quality, the fluorescence data were used for the EXAFS analysis following the procedures described in Ref. 3. Typical Fourier transforms of $k^3\chi(k)$ $\{\chi(k) = [\mu(k)-\mu_0]/\mu_0$, $\mu(k)$ is the absorption coefficient, μ_0 is the atomic absorption coefficient, and k is the wave vector$\}$ are given in Figs. 2(a) and 2(b).

As the cluster size was decreased from 15 to 7 Å, there was an increase in the contribution from the Cu-dimer spectrum. The Cu—Cu bond distance in the dimer is found to be 2.23 ±0.02 Å. This is in excellent agreement with the values reported in the literature for Cu_2 in the gas phase.[7] The Fourier transform of the EXAFS signal for 7-Å–mean-diameter particles is given in Fig. 3.

As mentioned at the beginning, we wish to find out details about the morphology of these microclusters. Since the data indicated the existence of a well-defined third-neighbor shell, a comparison was made with several models of crystallite structures, from fcc to icosahedra, in Table I. Since the fraction of atoms at the surface increases as the cluster size is decreased, one would expect a decrease in average coordination

TABLE I. Comparison of near-neighbor distances and coordination numbers for some common metallic crystal structures and icosahedral packing for clusters with a selected number of atoms.

Structure	First shell d[d]	N	Second shell d	N	Third shell d	N
fcc (55)[a]	1.00	7.85	1.4141	3.28	1.732	9.6
bcc (59)[b]	1.00	5.424	1.15	3.864	1.63	5.69
hcp (51)	1.00	7.765	1.41	3.059	1.63	1.02
Icosahedra (13)	1.0	1.846	1.70	4.615	2.00	0.923
	1.05	4.615				
Icosahedra (55)	1.0	3.05	(1.45)[e]	2.18	1.79	4.364
Mackay	1.05	5.42	1.70	4.364	1.97, 2.00	7.20
Cu particles,[c]	1.00	6 ± 1	1.42	3 ± 1	1.73	5 ± 1
experimental	(2.54 ±0.01 Å)		(3.57 ±0.01 Å)		(4.45 ±0.02 Å)	

[a] 55-atom fcc cluster consists of eight elementary unit cells with corner capped off.

[b] 59-atom bcc cluster consists of eight elementary unit cells with additional atoms at the body centers of neighboring cells.

[c] Cu clusters of 10 Å average diameter.

[d] Distances are normalized to the nearest-neighbor distance (atomic diameter).

[e] This distance appears only in an unrelaxed icosahedron.

TABLE II. Average atomic coordination numbers for fcc clusters of 13–55 atoms compared to experimentally measured values (error in parentheses) for Cu particles of 10 Å average diameter.

	First shell	Second shell	Third shell
13 atoms	5.54	1.85	3.69
19 atoms	6.32	1.89	5.05
43 atoms	7.256	3.07	8.93
55 atoms	7.85	3.273	9.6
Cu particles	6(1)	3(1)	5(1)
Cu metal	12	6	24

number or average number of bonds per Cu atom. The calculated results are shown in Table II for spherical fcc clusters of complete shells, consisting of 13, 19, 43, and 55 atoms, and compared to bulk Cu metal. The 55-atom Mackay icosahedron is given in Table I; the relaxed icosahedron will not show the 1.45 distance (in units of atomic diameter).[8] Simple inspection of Table I reveals that the fcc structure is the only one consistent with the observed interatomic distances. While the interatomic distances agree very well with the fcc model, the numbers of bonds are found to be smaller than the predicted values. This is in part due to the fact that the observed particles are not of uniform size, i.e., 19- to 55-atom clusters will contribute to the observed EXAFS. However, the average coordination number for the third shell is still significantly less than expected.

In deducing the coordination number from the EXAFS analysis, it is important to recognize that its value is highly correlated to the various parameters in the EXAFS equation.[3] These parameters include dynamic disorder described by a Debye-Waller–type term and an electron mean free path. A careful self-consistent fitting procedure was adopted to deduce the coordination number for each of the copper microclusters and for the metallic copper. The coordination number obtained from this analysis for various shells is smaller than that predicted by the fcc model and the deviations are outside the error bars of the above analysis for the third shell (even when taking the average coordination from 19- to 55-atom clusters). This reduction in the coordination number in the third shell is consistent with the presence of vacancies on the surface (missing atoms). Our calculations indicate that the third-nearest-neighbor (3nn) coordination numbers are more sensitive to surface vacancies than for 1nn or 2nn. This number drops from 9.6 for 55-atom clusters to 3.69 for thirteen atoms, where as 1nn changes from 7.85 to 5.54 and 2nn from 3.273 to 1.85. A deviation from spherical symmetry is also possible and will cause a change in coordination,[9] but also will affect the interatomic distances; missing atoms on the surface of the cluster are the most plausible explanation.

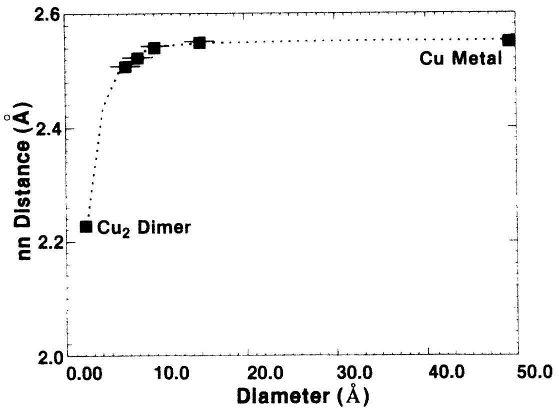

FIG. 4. Variation in interaction distance as a function of particle size.

Figure 4 shows the variation in nearest-neighbor distances as a function of the mean particle diameter. The contraction of atomic separation in the dimer Cu_2 is significant. In our studies we did not detect Cu_3 and Cu_4, probably because of their poor stability. The microclusters made up of thirteen or more atoms (5 Å or larger) seem to be stable and have an fcc structure. In these clusters the near-neighbor distances are very close to that of the bulk. These results are in good agreement with earlier electron microscopy measurements (although they were made on larger clusters) and with reported near-neighbor distances for highly dispersed Cu catalysts.[10] The discrepancy between the near-neighbor distances reported here and those of earlier EXAFS work on Cu deposited on carbon[11] may be attributed to the presence of very small multimers in these samples and/or interaction of microclusters with residual gases in the carbon support.

Recently, it has been noted from the electron diffraction of argon clusters that the atomic arrangement is different from the fcc structure of solid Ar.[8] There is strong evidence that these clusters have a structure based on polyicosahedra. On the other hand, our results on Cu clusters provide a direct evidence for the presence of a fcc structure of about thirteen atoms. It is likely that metallic clusters stabilize with their fundamental bulk interaction distances at a very early stage in their growth. Only very small stable molecules (Cu_2) will show appreciable deviation from the bulk interatomic distances.

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