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[11] From our data we determine $\mu\tau_0 \simeq (7\times 10^{-12}\ \mathrm{cm^2/V})y^{-1}$, where y is the quantum efficiency for generating free carriers at 2.14 eV. A value ~ 0.5 has been obtained for y. See C. Main and A. E. Owen, in *Electronics and Structural Properties of Amorphous Semiconductors*, edited by P. G. LeComber and J. Mort (Academic, New York, 1973), p. 527.

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Extended X-Ray–Absorption Fine Structure of Small Cu and Ni Clusters: Binding-Energy and Bond-Length Changes with Cluster Size

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(Received 23 April 1979)

Extended x-ray–absorption fine-structure measurements have been made on metal clusters of Cu and Ni which were formed by vapor deposition on amorphous carbon substrates. Small clusters of both elements show a substantial contraction of the nearest-neighbor metal-metal distance and an increase in binding energy for the onset of the K absorption edge. The results are explained by the increasing surface-to-volume ratio as the cluster size decreases resulting in a more free-atom–like configuration of the metal atoms.

Because of the importance of supported metallic microclusters as commerical catalysts,[1] model studies which elucidate their physical and electronic properties are highly desirable. Experimental data of the past two decades have conflicted as to the existence of bond-length changes in small particles.[2] All experiments we know of have determined lattice contractions or expansions as a function of particle size (or thin-film thickness or crystallite dimension) by the displacement of x-ray or electron Bragg-diffraction peaks.[2] The diffraction measurements were analyzed by referencing the observed pattern to an assumed lattice (i.e., the bulk) structure. Recently, a theoretical modeling study by Briant and Burton[3] has cast doubt on the so-determined values for nearest-neighbor distance contractions in small clusters. Thus, to elucidate whether the structures of small metallic particles or thin films are different from the bulk ones, a new method of small-cluster analysis is needed.

We have chosen the extended x-ray–absorption fine-structure technique (EXAFS)[4] to study the interatomic distances of atoms in small clusters of Cu and Ni. The advantage is that the analysis of EXAFS data is independent of crystal structure and is applicable to materials with no long-range order. In this Letter, we report the first direct evidence for bond-length contractions as a function of decreasing cluster size of Cu and Ni and extend measurements to sizes smaller than possible by other techniques. The preparation method and the substrate employed allow the study of the inherent characteristics of the metal particles in contrast to conventional small metal catelysts where interaction between the metal and substrate atoms may be significant.[5]

Experiments were done at the Standord Synchrotron Radiation Laboratory (SSRL) on the storage ring SPEAR. The EXAFS spectra were recorded with use of fluorescence detection[6] to enhance the signal-to-background ratio. Cluster samples were formed by evaporating multiple layers of metal and carbon onto 5000-Å polymer films, several of which were stacked together. Uniformity of particle size was achieved by controlling the amount of deposited material with a quartz-crystal detector and feedback circuit. Carbon interlayers ~ 50–100 Å thick were used to separate the various layers of evaporated metal clusters and to protect the clusters from reaction with air. Transmission electron microscopy was used to characterize clusters which were large enough to be visible.[7]

The spectra obtained for Cu are shown in Fig. 1; spectra for Ni are similar. They extend over the range from bulk metals and bulklike clusters at heavy evaporated coverages to few-atom clusters or isolated single atoms at low coverages. In the following we shall analyze the spectra in terms of the K-edge threshold and extended absorption fine structure.

The K-edge threshold energies for Cu and Ni versus coverage are plotted in Figs. 2(a) and 2(b), respectively. For Cu, the K-edge threshold remains identical with that of the bulk metal down to very low coverages (~ 8×10^{15} atoms/cm^2) corresponding to a particle size of ~40–45 Å in diameter. Thereafter, an increase in binding energy is observed up to ~ 0.7 eV at our lowest coverage, 8×10^{14} atoms/cm^2, a particle size which is below the limits of detection by transmission electron microscopy. For Ni, we observe a much more pronounced energy shift of the K edge, beginning at a "continuous" film[8] region. Between the highest and the lowest evaporated coverages the edge shifts by ~ 1.3 eV.

The changes in nearest-neighbor separations in the metal clusters exhibit a close correspondence to the changes in the K-edge threshold. In Fig. 2 we have plotted the nearest-neighbor metal-metal distance against the evaporated coverage

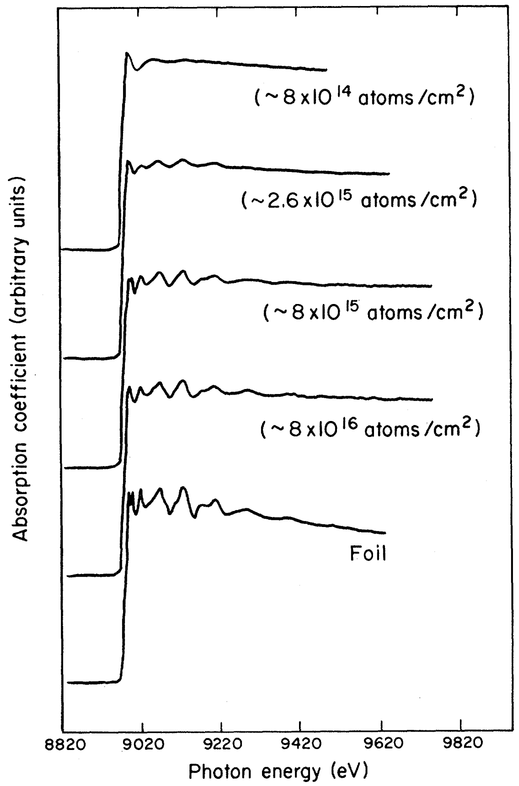

FIG. 1. EXAFS spectra of Cu for a series of evaporated coverages and bulk foil. The bulk spectrum was recorded in the transmission mode.

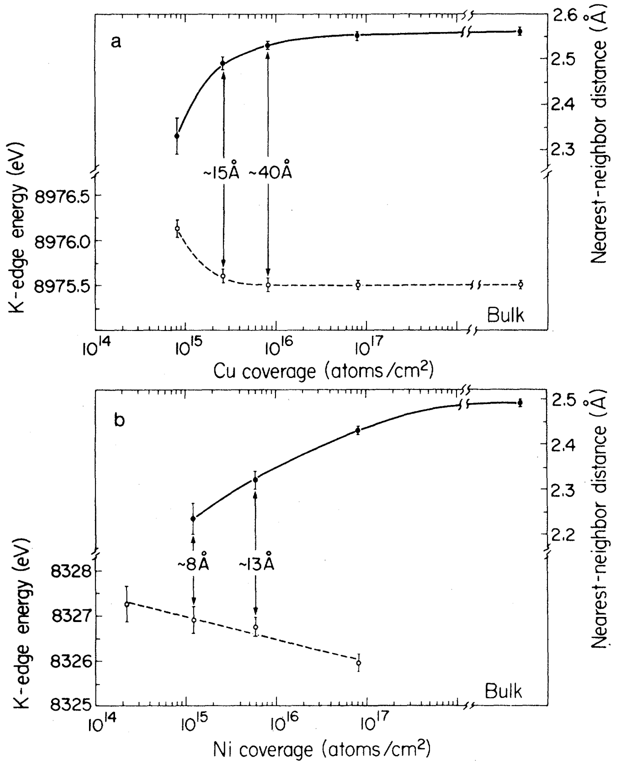

FIG. 2. (a) Cu-Cu nearest-neighbor distance as a function of evaporated coverage (solid line). Relative change in the onset of the K-edge energy as a function of evaporated coverage (dashed line). (b) Same as (a) for Ni. The lowest Ni coverage is indicative of atomic dispersion (no Ni-Ni nearest neighbors are detectable). The bulk Ni spectrum was recorded under different experimental conditions, thus precluding a comparison of K-edge energy.

with the bulk value representing our Fourier-transformed radial distribution function increased by a phase shift ($\alpha_{\text{Cu}} = 0.33$ Å; $\alpha_{\text{Ni}} = 0.28$ Å). These shifts are applicable to all coverages of a given element in which the nearest neighbor remains the same element, by chemical transferability.[9] As for the K-edge threshold, the Cu-Cu neighbor distance remains constant for coverages above 8×10^{15} atoms/cm^2, then shows a pronounced contraction of a total of ~ 9% at the lowest coverage. At this coverage a Cu-C distance peak is observed in the Fourier transform which is clearly distinguishable from the Cu-Cu distance peak. The Ni-Ni nearest-neighbor distances change differently from the Cu-Cu ones and show noticeable contraction beginning at higher coverage, closely following the trend in the K-edge threshold shifts. The contraction is seen at a coverage (~ 8×10^{16} atoms/cm^2) which appears in the microscope as a "continuous" film.[8] At the lowest Ni coverage, only one radial-distribution-function peak at short bond distance is observed, which we attribute to Ni-C neighbors, indicating that the Ni is atomically dispersed. The Ni-C peak falls at ~ 0.7 Å shorter distance in the Fourier transform than the Ni-Ni peak and hence, can be readily distinguished from the latter.

The decrease of the EXAFS amplitude relative to the K-edge jump seen in Fig. 1 is mostly due to the fact that at the lower coverages only a small fraction of the evaporated metal atoms are in the form of clusters on the graphite surface. Most metal atoms are incorporated into the substrate as isolated atoms and therefore, contribute to the total absorption but not to the EXAFS amplitude, because of scattering within the clusters. Analysis of the EXAFS phases did not reveal any effects expected from an increase in the disorder[10] with decreasing cluster size, which leads us to believe that the observed contractions are real and within the error bars shown in Fig. 2.

The contraction for a known average particle size is *larger* in Ni than in Cu. This is illustrated in Fig. 3 where we plot the percent lattice contraction as a function of the reciprocal diameter of various-sized particles. In each case within the statistics of the data, we observe the lattice contraction to scale approximately as the surface-to-volume ratio ($1/d$). At the lowest coverages of our experiment for Cu and the second lowest coverage for Ni, the metal-metal nearest-neighbor distances are 2.33 ± 0.04 Å and 2.24 ± 0.04 Å, respectively. Experimentally, the bond length for gas-phase Cu_2 is 2.22 Å,[11] whereas that calculated by Anderson is 2.26 Å.[12] No experimental bond-length data seen to exist for Ni_2; however, Anderson estimates it to be ~ 2.21 Å.[13] Upton and Goddard[14] calculate a shorter bond length for Ni_2 of 2.04 Å. Our results compare favorably and show that at the lowest coverages the metal-metal

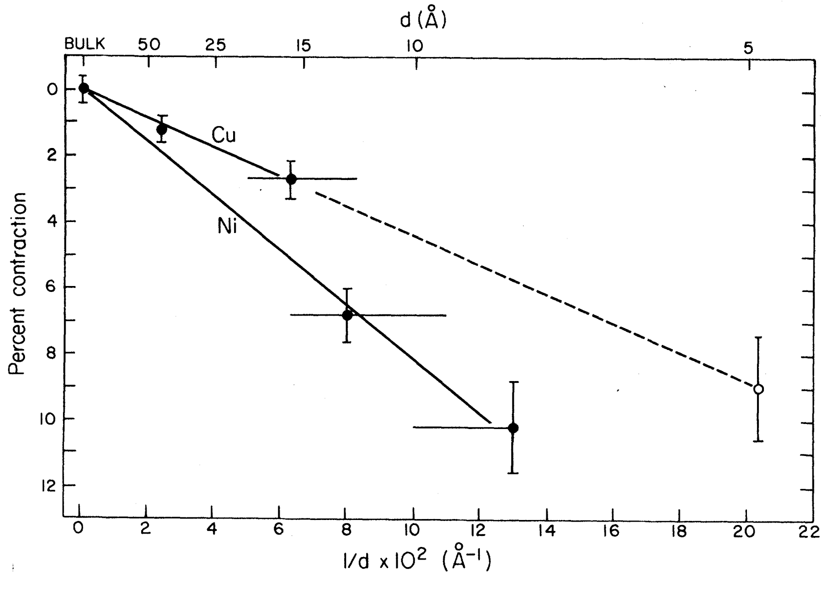

FIG. 3. Plot of percent decrease in nearest-neighbor interatomic distance vs the reciprocal average diameter, d, of various-sized Cu and Ni clusters. The dashed line extrapolates the $1/d$ dependence to the observed percent contraction for the lowest Cu coverage where clusters are too small to be characterized.

distances approach those expected for diatomic or slightly larger clusters.

The observed changes in the K-edge threshold energy as a function of cluster size are attributed to core-level binding-energy shifts relative to the Fermi level. Shifts similar to the ones reported here were previously observed by Mason *et al.*[15] with use of x-ray photoemission. Changes in binding energy between atoms incorporated in a metal and isolated atoms arise from changes in electronic configuration[16] caused by the renormalization of valence electron charge.[17] On forming the metal there is a flow of charge into the volume appropriate to the Wigner-Seitz cell, leading to a charge compression with the result that the binding energy is *smaller* in the bulk metal than in the free atom. For small clusters where a significant fraction of the atoms are located in surface sites, a "net" binding energy intermediate between the free atom and bulk-metal value is expected. This is borne out by the calculations of Fulde, Luther, and Watson[18] and agrees with our results, which show an increased (or more free-atom–like) binding energy for small cluster sizes.

The observed bond-length contraction with decreasing cluster size can also be explained by the aforementioned redistribution of charge.[19] In a surface the number of nearest-neighbor atoms is significantly less in the bulk, which leads to a reduction in repulsive interactions between nonbonded electron pairs.[12,14] A contraction of nearest-neighbor distance is the result.

In our discussion, we have ignored any metal-substrate interaction. Cu does not form a stable carbide and neither does Ni at room temperature. Photoemission valence-band spectra of samples which were prepared identically to the ones used for the present study were characteristic of those of the clean metals. Furthermore, the metal-metal bond length in a carbide is expected to be *larger* than in the pure metal. The close correspondence between bond length and binding-energy changes further establishes the latter to be an *initial*- rather than a *final*-state effect. Thus, we can exclude a change in substrate-related extra-atomic relaxation to be the source of the observed binding-energy shifts.

The present investigation establishes, for the first time unambiguously, *systematic* nearest-neighbor bond-length changes with cluster size. The contractions found for small clusters correspond well with expectations based on previous theoretical calculations down to coverages which correspond essentially to diatomic molecules. The observed changes in the K-edge threshold closely follow the observed changes in the nearest-neighbor distances, as expected from theory, and agree well with previous photoemission results.

We thank B. F. Nellis for help with sample preparation, M. G. Mason for helpful discussions, and P. H. Fuoss for providing the bulk nickel EXAFS data. We thank P. Eisenberger and E. A. Stern for discussions concerning the effects of disorder on the EXAFS analysis.

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Microwave-Enhanced Proximity Effect in Superconductor–Normal-Metal–Superconductor Microjunctions

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(Received 8 February 1979)

Very large microwave enhancements of the critical current of small superconductor–normal-metal–superconductor junctions have been observed to temperatures as low as $0.2T_c$ of the superconductor. The experimental results indicate that this enhancement is due to a strengthening of the proximity effect at the center of the normal-metal layer by the time-varying field.

Microwave-induced enhancement of the critical current (I_c) of superconducting microbridges has been studied in great detail,[1,2] and it is widely believed that the physical mechanism underlying this enhancement is an increase in the superconducting energy gap due to a change in the quasiparticle energy distribution by the applied microwave field.[3,4] But all previous experiments have used microbridges in which all of the components are either below[1] or near[2] their superconducting transition temperature.

In this Letter we report the first observations of very large microwave-induced increases in the zero-voltage current through superconductor–normal-metal–superconductor (SNS) microjunctions, that is, microbridges in which the bridge is of a metal (copper) which is not superconducting at temperatures as low as 0.001 K. For an appropriate sample this enhancement can be seen at all accessible temperatures below the transition temperature of the superconducting electrodes (1.5 K$<T<$7.26 K), and over much of this temperature range the increase can be several orders of magnitude. We have examined this effect over nearly two decades in microwave frequency and over a decade in bridge length. Criteria for the minimum microwave frequency necessary for enhancement have been determined, as has the dependence of the degree of enhancement on the bridge length. Our experimental results strongly indicate that the critical-current enhancement is due to a strengthening of the superconducting proximity effect at the center of the normal-metal bridge by the time-varying electric field.

The SNS junctions were prepared in the variable-thickness microbridge geometry using electron and photon lithography; the fabrication details have been presented elsewhere.[5] The bank electrodes were of lead, the bridges of copper. The bridge thickness D ranged from 60 to 150 nm, the width W from 0.2 to 1.0 μm, the length L from 0.2 to 2.0 μm; low-temperature bridge resistances ranged from 0.1 to 1 Ω.

In the absence of applied microwaves I_c was found to have the quasiexponential temperature dependence expected of SNS tunnel junctions. The zero-voltage tunnel current first became observable at a temperature somewhere below T_c of the lead electrodes (7.26 K); this onset temperature was progressively lower the longer the junction. For T well below T_c the temperature dependence of I_c was found to be well described, both in functional form and in amplitude, by calculations based on the microscopic equations of Usadel.[6] This is illustrated in Figs. 1 and 2, where the temperature dependence of I_cR for two different samples is compared with theoretical predictions obtained in a manner similar to that employed by