

## Electronic Structure of Copper Particles Supported on TiO<sub>2</sub>, Graphite, and Al<sub>2</sub>O<sub>3</sub> Substrates: A Comparative Study

A. F. CARLEY, M. K. RAJUMON, AND M. W. ROBERTS

*School of Chemistry and Applied Chemistry, University of Wales, College of Cardiff,  
P.O. Box 912, Cardiff CF1 3TB United Kingdom*

Received December 4, 1992; accepted December 23, 1992

IN HONOR OF SIR JOHN MEURIG THOMAS ON HIS 60TH BIRTHDAY

X-ray photoelectron spectroscopy (XPS) and X-ray induced Auger electron spectroscopy (XAES) have been employed to investigate the electronic structure of copper particles deposited on TiO<sub>2</sub>, graphite, and Al<sub>2</sub>O<sub>3</sub> substrates. While at high coverages the spectral features are similar to those of bulk Cu, at low coverages these features are sensitive to both cluster size and final state relaxation effects. We have estimated the effective coulomb interaction energy,  $U_{\text{eff}}$ , between the two holes created in the valence band as a result of the Auger process, and observe that it is strongly dependent on the substrate and the neighboring Cu atoms. © 1993 Academic Press, Inc.

### 1. Introduction

Small metal particles are a subject of great interest because of their technological importance, especially in heterogeneous catalysis (1-4). Due to the finite number of atoms in the clusters, their electronic structure represents a transition state between the discrete energy levels of free atoms and the continuous bands of bulk metals. There have been a number of studies of metal clusters supported on various substrates (1, 5); in this paper we investigate copper clusters.

The most powerful techniques employed to investigate the electronic structure of small metal particles dispersed on various substrates are X-ray photoelectron spectroscopy (XPS) and X-ray excited Auger electron spectroscopy (XAES), especially where Auger emission involves the valence band. A combination of these two techniques has been effectively used (6-8) to study both the initial state effects (cluster

size, charge state of the atom in question) and final state relaxation effects. The quasi-atomic nature of the  $L_3M_{45}M_{45}$  Auger spectrum of metallic Cu has been discussed in the literature (9-11), the quasi-atomic characteristics being attributed to the fact that the effective coulomb interaction,  $U_{\text{eff}}$ , between the two holes in the valence band, as a result of the Auger emission, is greater than twice the valence band width ( $U_{\text{eff}} > 2W$ ).

When a core hole is produced in a free atom, the outer electrons relax towards it, this screening resulting in an intratomic relaxation shift  $R_{\text{ia}}$  in the kinetic energy of the outgoing photoelectron. In the solid state the valence and conduction electrons surrounding the atom with the core hole also respond so as to screen the hole, leading to the extratomic relaxation shift,  $R_{\text{ea}}$ . Antonides *et al.* (6) have estimated  $R_{\text{ia}}$  and  $R_{\text{ea}}$  for several metals including Cu, and observed that  $R_{\text{ea}}$  is much larger than  $R_{\text{ia}}$  indicating that a large contribution to the total relax-

ation energy comes from the surrounding atoms and valence electrons.

$U_{\text{eff}}$  can be estimated from the Cu( $L_3M_{45}M_{45}$ ) kinetic energy, Cu( $2p_{3/2}$ ) and Cu( $3d$ ) binding energies from Eq. (1)

$$E_K(L_3M_{45}M_{45}) = E_C - 2E_V - U_{\text{eff}}, \quad (1)$$

where  $E_C$  is the binding energy of the core level ( $2p_{3/2}$ ) and  $E_V$  the binding energy of the valence level ( $3d$ ) involved in the transition.  $U_{\text{eff}}$  in metallic Cu is strongly reduced from the free atom value because of the extraatomic relaxation process in the condensed state.

In the case of supported metal clusters, the neighboring atoms and the substrate conduction electrons are responsible for the extraatomic relaxation. If the substrate is a poor conductor then its contribution to extraatomic relaxation will be much smaller. Recently Kohiki (7) has carried out studies of small Pd clusters deposited on Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> substrates. He has attributed changes in the electronic structure of the Cu clusters to both cluster size effects and to extraatomic relaxation effects which are directly correlated with the polarizability of the substrates.

Following Wagner (12), we consider first the changes in  $E_C$  and  $E_V$  on going from the free atom (a) to the solid state (s)

$$\Delta E_C^{\text{as}} = \Delta V^{\text{as}} - \Delta R^{\text{as}}(L^+) \quad (2)$$

$$\Delta E_V^{\text{as}} = \Delta V^{\text{as}} - \Delta R^{\text{as}}(M^+) \quad (3)$$

where  $\Delta V^{\text{as}}$  represents the difference in the initial state charge distribution and  $\Delta R^{\text{as}}$  the difference in the final state *extraatomic* relaxation energy corresponding to a core hole ( $L^+$ ) and a hole in the valence band ( $M^+$ ), as indicated. The *intraatomic* relaxation term is not included since it is expected to be the same for the free atom and the condensed state.

If we assume the solid to be a continuous medium, we can approximate the extraatomic relaxation shift by the polarization energy  $E_p$ . For a single core hole

$$E_p(L^+) \sim e^2/r,$$

where the radius  $r$  defines the minimum electron screening distance. In the case of two valence holes, assuming the same value for  $r$ , we have

$$\begin{aligned} E_p(M^+M^+) &\sim (2e)^2/r \\ &= 4e^2/r = 4R^{\text{as}}(L^+). \end{aligned}$$

Now,  $R^{\text{as}}(M^+) = E_p(M^+) = E_p(M^+M^+)/2 = 2E_p(L^+) = 2R^{\text{as}}(L^+)$ . Thus

$$\Delta E_V^{\text{as}} = \Delta V^{\text{as}} - 2\Delta R^{\text{as}}(L^+). \quad (4)$$

From Eqs. (1), (2), and (4) we obtain for  $\Delta E_K$

$$\begin{aligned} \Delta E_K^{\text{as}}(LMM) &= -\Delta V^{\text{as}} + 3\Delta R^{\text{as}}(L^+) \\ &\quad - (U_{\text{eff}}^a - U_{\text{eff}}^s) \end{aligned} \quad (5)$$

Equations analogous to (2) and (5) hold for the changes in  $E_K$  and  $E_B$  between free atom (a) and cluster (c). We are interested here in  $\Delta E_B^{\text{cs}}$  and  $\Delta E_K^{\text{cs}}$  which are given by

$$\begin{aligned} \Delta E_K^{\text{cs}} &= \Delta E_K^{\text{as}} - \Delta E_K^{\text{ac}} \\ &= (-\Delta V^{\text{as}} + \Delta V^{\text{ac}}) + 3(\Delta R^{\text{as}} - \Delta R^{\text{ac}}) \\ &\quad + (U_{\text{eff}}^s - U_{\text{eff}}^c) \end{aligned}$$

$$\begin{aligned} \Delta E_B^{\text{cs}} &= \Delta E_B^{\text{as}} - \Delta E_B^{\text{ac}} \\ &= (\Delta V^{\text{as}} - \Delta V^{\text{ac}}) - (\Delta R^{\text{as}} - \Delta R^{\text{ac}}). \end{aligned}$$

The usefulness of the Auger parameter, defined by  $\alpha = E_B + E_K$ , has been described elsewhere (12). The change in  $\alpha$  between the cluster and the solid is given by  $\Delta\alpha^{\text{cs}}$

$$\begin{aligned} \Delta\alpha^{\text{cs}} &= \Delta E_B^{\text{cs}} + \Delta E_K^{\text{cs}} \\ &= 2(\Delta R^{\text{as}} - \Delta R^{\text{ac}}) - U_{\text{eff}}^c - U_{\text{eff}}^s \end{aligned}$$

$$\text{or } \Delta\alpha^{\text{cs}} = 2\Delta R^{\text{cs}} - \Delta U_{\text{eff}}^{\text{cs}}. \quad (6)$$

In the present paper, we have made a comparative study of the dispersion of Cu particles on TiO<sub>2</sub>, graphite, and Al<sub>2</sub>O<sub>3</sub> substrates using a combination of XPS and XAES techniques. The spectral features are discussed on the basis of cluster size and final state relaxation effects.

## 2. Experimental

Electron spectroscopic measurements were performed using a VG electron spec-

trometer with separate sample preparation and analyzer chambers, the details of which have been described elsewhere (13). The Ti and Al foils and the graphite sample were mounted on a stainless steel sample holder and cleaned by cycles of heating and Ar<sup>+</sup> ion etching. To obtain a thick layer of Al<sub>2</sub>O<sub>3</sub>, the Al foil had to be heated overnight at 805 K in a few Torr of oxygen, whereas a TiO<sub>2</sub> overlayer of desired thickness was obtained by heating Ti in oxygen at 700 K (10<sup>-4</sup> Torr, 3 hr). The thickness of the oxide layers was calculated from the observed attenuation of the substrate photoelectron signals from the respective samples. Copper was deposited by resistive heating from a molybdenum filament; during the deposition and the course of the experiments the substrate was kept at room temperature. In the low coverage region, the Cu concentration on the surface was estimated using the method described by Carley and Roberts (14) while in the high coverage region the thickness of the Cu overlayer was estimated from the attenuation of the Ti(2*p*), Al(2*p*), and C(1*s*) signals after deposition of Cu. Since our interests were mainly in the low coverage regime, and also to obtain a better Cu(L<sub>3</sub>M<sub>45</sub>M<sub>45</sub>) Auger signal intensity at low coverages, we used 60 eV pass energy for Auger measurements whereas the pass energy for photoelectron measurements was 20 eV. MgK<sub>α</sub> radiation (1253.6 eV) was used as the source energy. The data acquisition and analysis of the spectra were carried out using software developed in this laboratory (15). The reference lines for energy calibrations were Ti(2*p*<sub>3/2</sub>) from TiO<sub>2</sub> (459.0 eV), Al(2*p*) from Al<sub>2</sub>O<sub>3</sub> (75.2 eV), and C(1*s*) from graphite (284.1 eV).

### 3. Results

#### 3.1. Copper Supported on TiO<sub>2</sub>

The L<sub>3</sub>M<sub>45</sub>M<sub>45</sub> Auger spectra of Cu deposited on a TiO<sub>2</sub> substrate are shown in Fig. 1 for various coverages. As seen from the figure, the spectrum for the lowest coverage

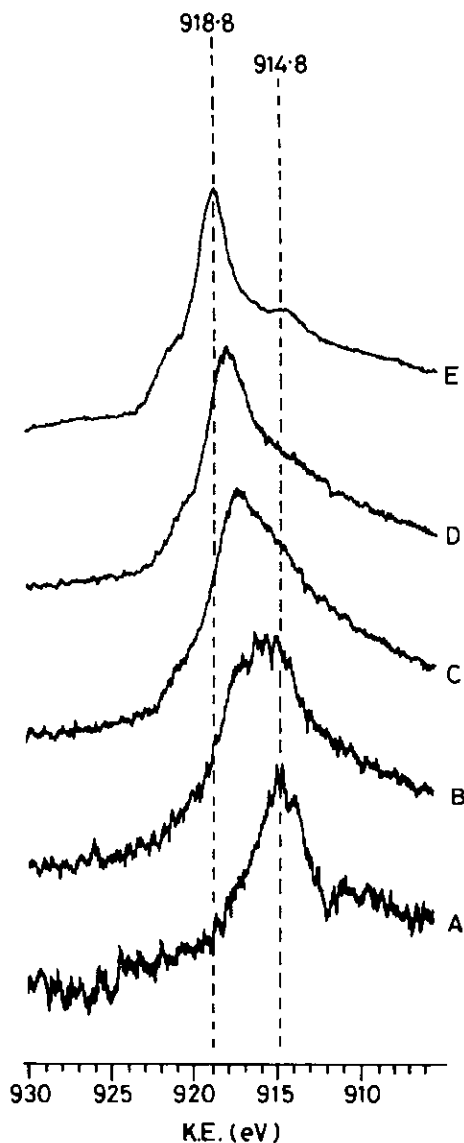


FIG. 1. Cu(L<sub>3</sub>M<sub>45</sub>M<sub>45</sub>) Auger spectra of Cu deposited to increasing extents (A-E) on a TiO<sub>2</sub> substrate. (A)  $\sigma_{\text{Cu}} = 7 \times 10^{13} \text{ cm}^{-2}$ ; (E)  $\sim 14 \text{ \AA}$  thick Cu layer.

(curve A;  $\sigma_{\text{Cu}} = 7 \times 10^{13} \text{ atoms cm}^{-2}$ ) appears at 914.8 eV compared with the bulk value of 918.8 eV. The spectrum at the lowest coverage is also much broader than that for bulk Cu. As the coverage is progressively increased (spectra B, C, and D) an additional peak develops on the higher kinetic energy side of the L<sub>3</sub>M<sub>45</sub>M<sub>45</sub> feature

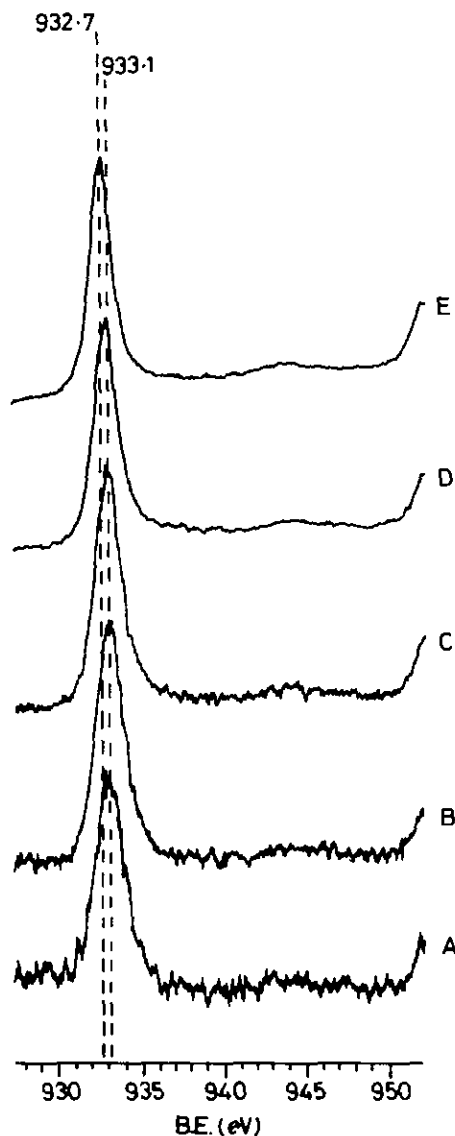


FIG. 2. Cu(2*p*) spectra of Cu deposited on a TiO<sub>2</sub> substrate (see Fig. 1 for details).

which grows in intensity and shifts further to higher kinetic energy; finally for a thick layer of copper (spectrum E;  $\sim 14$  Å) the spectrum is similar to that of bulk copper. The final state multiplets observed in the spectrum of metallic Cu are not clearly resolved for low coverages of copper present on TiO<sub>2</sub>. The Cu(2*p*<sub>3/2</sub>) line for the above coverages are shown in Fig. 2. We have

observed a small decrease in the fwhm (full width at half maximum) from 2 eV to 1.7 eV and a downward shift of 0.4 eV in the binding energy of the Cu(2*p*<sub>3/2</sub>) line as the coverage is increased from  $7 \times 10^{13}$  atoms cm<sup>-2</sup> to an  $\sim 14$  Å thick Cu layer. In Fig. 3 we show the valence band difference spectra for various stages of Cu deposition; the difference spectra are obtained by subtracting the TiO<sub>2</sub> spectrum from those of the various Cu deposited on TiO<sub>2</sub> surfaces. This enables us to locate the *d*-band maximum for different coverages. It should be noted that  $\Delta E_V$  between the smallest coverage and a thick layer of copper is only 0.5 eV. A marked decrease in the Cu *d*-band width is also noticed with decreasing Cu coverage (see Fig. 3). The fwhm of the smallest coverage ( $\sigma_{\text{Cu}} = 7 \times 10^{13}$  atoms cm<sup>-2</sup>) is only 1.9 eV compared with the value of 2.7 eV for bulk Cu ( $\sim 14$  Å). The estimated values of  $\alpha$ ,  $U_{\text{eff}}$ , and the various energy values are tabulated in Table I.

### 3.2. Copper Supported on Graphite

In Fig. 4 are shown the Cu(*L*<sub>3</sub>*M*<sub>45</sub>*M*<sub>45</sub>) Auger spectra of Cu deposited on a clean graphite substrate for various coverages. For a very low coverage of Cu (curve A;  $\sigma_{\text{Cu}} = 3 \times 10^{13}$  atoms cm<sup>-2</sup>), the shift in the Auger line is only 1.3 eV towards lower kinetic energy compared with the bulk value (curve B;  $\sim 14$  Å thick Cu layer). The spectrum at low coverage is much broader but the line shape is similar to that of bulk Cu. The binding energy values of Cu(2*p*<sub>3/2</sub>) and Cu(3*d*) levels, and the *L*<sub>3</sub>*M*<sub>45</sub>*M*<sub>45</sub> Auger kinetic energy values along with the Auger parameter and  $U_{\text{eff}}$  are listed in Table II. The copper *d*-band is narrower at low coverages (curve A; fwhm = 2.1 eV at  $\sigma_{\text{Cu}} = 3.4 \times 10^{13}$  atoms cm<sup>-2</sup>) compared to 2.7 eV for the bulk Cu (curve B;  $\sim 14$  Å), whereas the Cu(2*p*) line is broader (fwhm = 2.3 eV) than for the "bulk" metal (fwhm = 1.7 eV). The value of  $U_{\text{eff}}$  is the same for both the smallest coverage and for the thick layer of Cu, and is smaller than that estimated for the Cu/TiO<sub>2</sub>

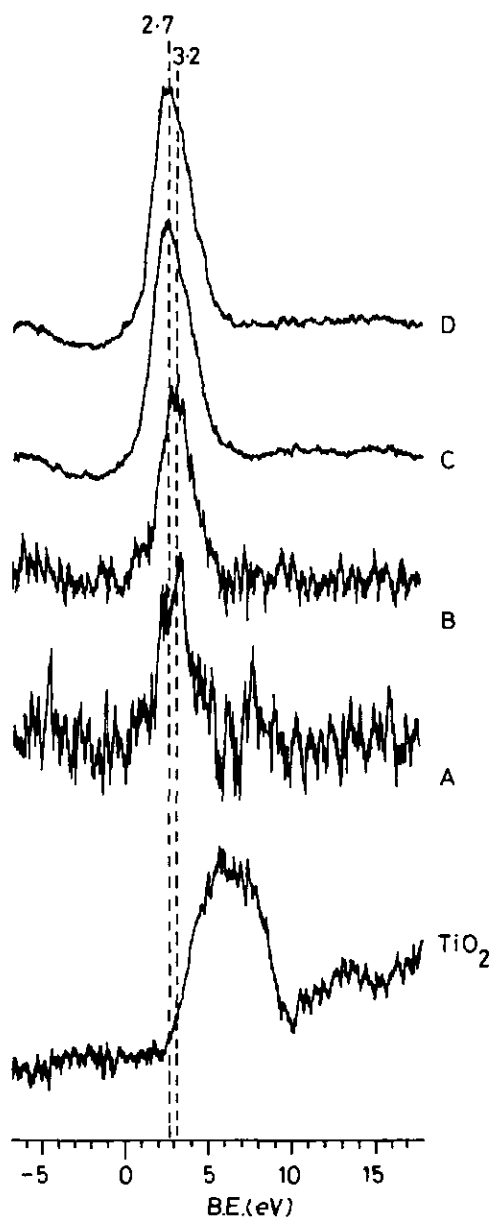


FIG. 3. Valence band (VB) difference spectra of Cu deposited to increasing extents (A-D) on a  $\text{TiO}_2$  substrate. (A)  $\sigma_{\text{Cu}} = 1.1 \times 10^{14} \text{ cm}^{-2}$ ; (B)  $\sim 14 \text{ \AA}$  thick layer. Also shown is the VB spectrum from "clean"  $\text{TiO}_2$ , used in the subtraction procedure.

surface. This result shows that the screening properties of bulk copper metal and copper clusters on a graphite substrate are very similar.

### 3.3. Copper Supported on Alumina

In Fig. 5 are shown the  $L_3M_{45}M_{45}$  Auger spectra of Cu deposited on the *in situ* grown  $\text{Al}_2\text{O}_3$  for various coverages. In the low coverage region the spectrum (Fig. 5, curve A) is broader and appears at a higher kinetic energy, 915.6 eV, compared with that of Cu on  $\text{TiO}_2$  at a similar coverage. In Table III the values of  $U_{\text{eff}}$ ,  $\alpha$ , and energies of the Auger and photoelectron lines are summarized. Unlike with Cu/ $\text{TiO}_2$  and Cu/graphite surfaces, we do not observe a significant narrowing of the *d*-band at low coverages of Cu present on the  $\text{Al}_2\text{O}_3$  substrate. The fwhm of the lowest coverage obtained ( $\sigma_{\text{Cu}} = 6 \times 10^{13} \text{ atoms cm}^{-2}$ ) is 2.5 eV and that of the bulk Cu is 2.7 eV. On the other hand the Cu( $2p_{3/2}$ ) spectrum broadens significantly at low coverages, the fwhm values being 2.3 and 1.7 eV respectively for coverages of  $6 \times 10^{13} \text{ atoms cm}^{-2}$  and  $\sim 14 \text{ \AA}$ .

## 4. Discussion

The extent to which the initial state, cluster size and final state relaxation processes influence the Auger and photoelectron lines has been discussed extensively in the literature. There is a general consensus that Auger spectra are more sensitive to these effects than are the photoelectron lines. Of the three substrates investigated, the largest shift observed in the kinetic energy at low coverages is with  $\text{TiO}_2$ . Moreover the fwhm of the Auger peak is smallest for this case. These observations can be correlated with electron microscopic studies (16), which have shown that metal dispersion is highest on  $\text{TiO}_2$  compared with  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ , and carbon. As the coverage of copper is increased we observe a shoulder developing on the higher kinetic energy side of the Auger spectrum (curve B, Fig. 1), reflecting the coalescence of small clusters. For high coverages of Cu the spectrum corresponds to that of bulk copper. De Crescenzi *et al.* (17) have recently studied cluster size effects on the line width of the Auger spectra of copper clusters on a graphite substrate

TABLE I  
MEASURED CORE AND VALENCE LEVEL BINDING ENERGIES, AUGER KINETIC ENERGIES FOR Cu DEPOSITED ON TiO<sub>2</sub>, AND DERIVED VALUES FOR THE AUGER PARAMETERS AND  $U_{\text{eff}}$  (SEE TEXT)

Surface coverage ( $\sigma$ )	$E_K(\text{Cu}L_3M_{45}M_{45})$	$E_B(\text{Cu}2p_{3/2})$	$E_B(3d)$	Auger parameter	$U_{\text{eff}}$
$7 \times 10^{13}$ atoms $\text{cm}^{-2}$	914.8	933.1	3.2	1847.9	11.9
$\sim 14$ Å thick Cu layer	918.8	932.7	2.7	1851.5	8.5

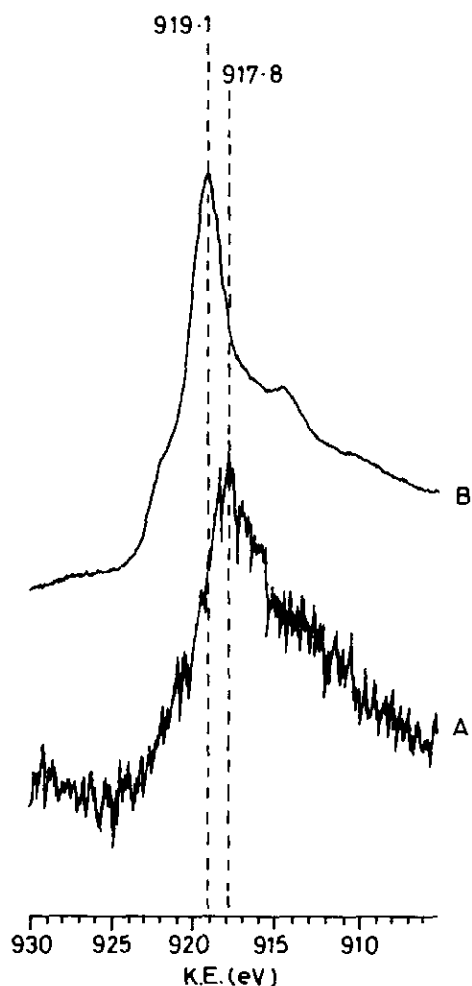


FIG. 4.  $\text{Cu}(L_3M_{45}M_{45})$  Auger lines of Cu deposited on a graphite substrate. (A)  $\sigma_{\text{Cu}} = 3 \times 10^{13}$   $\text{cm}^{-2}$ ; (B)  $\sim 14$  Å thick Cu layer.

and have attributed the broadening of the  $\text{Cu}(L_3M_{45}M_{45})$  Auger line to the presence of a range of cluster sizes.

The large variation in the Auger kinetic energy compared with the photoelectron binding energy can be understood from Eq. (5). The two valence band holes in the final state after the  $L_3M_{45}M_{45}$  Auger process are less effectively screened in the case of small clusters leading to increased hole-hole repulsion and a higher value of  $U_{\text{eff}}$ . The estimated value of  $U_{\text{eff}}$  is greatest in the case of Cu/TiO<sub>2</sub>, (see tables), suggesting that for TiO<sub>2</sub> copper is more efficiently dispersed, giving rise to very small clusters compared with the other two substrates. Moreover, the relatively narrow Auger line in the Cu/TiO<sub>2</sub> system, at the lowest coverage, suggests a more or less uniform cluster size distribution. At high coverages of Cu on all the three substrates, the spectra are similar showing the multiplet features and energy values expected for the bulk metal. We have evaluated  $\Delta U_{\text{eff}}$  and  $\Delta R$  between the lowest and highest coverages of Cu on TiO<sub>2</sub>, graphite and Al<sub>2</sub>O<sub>3</sub> using Eqs. (1) and (6), and the values are shown in Table IV. Bhal *et al.* (18) have estimated the contribution due to the initial state charge distribution and relaxation effects in the case of Pt deposited on a SrTiO<sub>3</sub>(100) surface, and obtained values of 0.5 eV for the initial state charge distribution and 0.8 eV for the relaxation shift. However, they neglected  $U_{\text{eff}}$  in estimating these values; it is, however, clear from Table IV that  $\Delta U_{\text{eff}}$  dominates the observed changes in  $\alpha$ . For poorly conducting sub-

TABLE II  
MEASURED CORE AND VALENCE LEVEL BINDING ENERGIES, AUGER KINETIC ENERGIES FOR Cu DEPOSITED ON GRAPHITE AND DERIVED VALUES FOR THE AUGER PARAMETERS AND  $U_{\text{eff}}$  (SEE TEXT)

Surface coverage ( $\sigma$ )	$E_K(\text{Cu}L_3M_{45}M_{45})$	$E_B(\text{Cu}2p_{3/2})$	$E_B(3d)$	Auger parameter	$U_{\text{eff}}$
$3.4 \times 10^{13}$ atoms $\text{cm}^{-2}$	917.8	933.3	3.3	1851.1	8.9
$\sim 14$ Å thick Cu layer	919.1	932.8	2.4	1851.9	8.9

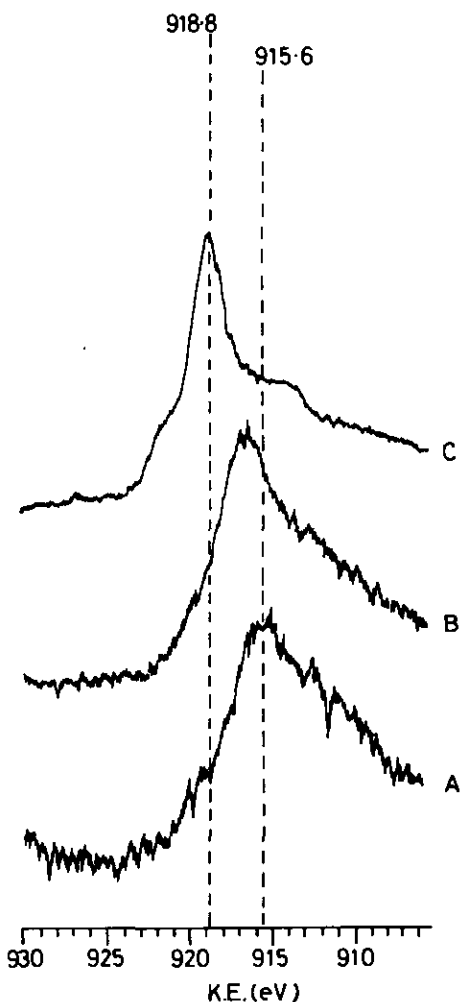


FIG. 5.  $\text{Cu}(L_3M_{45}M_{45})$  Auger lines of Cu deposited on an  $\text{Al}_2\text{O}_3$  substrate. (A)  $\sigma_{\text{Cu}} = 6 \times 10^{13}$   $\text{cm}^{-2}$ ; (B)  $\sigma_{\text{Cu}} = 1.8 \times 10^{14}$   $\text{cm}^{-2}$ ; (C)  $\sim 14$  Å thick Cu layer.

strates, the major factor affecting the Auger kinetic energy of the Cu Auger line is  $U_{\text{eff}}$  which in turn depends on the dispersion of the Cu clusters.

The fwhm and binding energy of the  $\text{Cu}(2p)$  level both increase as we go from the bulk metal to small clusters with the observed concomitant narrowing of the  $\text{Cu}(3d)$ -band providing a clue to the explanation of the latter. The  $d$ -band narrowing reflects a decrease in  $d$ -electron density per atom, which results in a shift from  $d$ -electron screening of the core hole to less effective screening by  $s$ - $p$  electrons (19). This leads to the observed positive binding energy shift in small clusters compared with bulk copper. The number of  $d$ -electrons per metal atom in a small cluster is smaller than that in the bulk because of intraatomic  $sp$ - $d$  hybridization (1). The increase in fwhm of the  $\text{Cu}(2p_{3/2})$  peak for small clusters is not so easily explained. It may reflect the range of cluster sizes present on the substrate, or may be due to an increase in natural linewidth. The latter would imply that the core hole has a shorter lifetime in the cluster than in bulk copper, an argument difficult to sustain when one considers the poorer screening of the hole in the cluster.

The relatively large shift in the  $L_3M_{45}M_{45}$  line is attributed to cluster size and relaxation effects. However, we must also consider the possibility that small clusters may interact with the oxide substrate and that there is a chemical contribution to the observed shifts. The standard free energy of formation of  $\text{Cu}_2\text{O}$  and  $\text{CuO}$  are much

TABLE III

MEASURED CORE AND VALENCE LEVEL BINDING ENERGIES, AUGER KINETIC ENERGIES FOR Cu DEPOSITED ON Al<sub>2</sub>O<sub>3</sub>, AND DERIVED VALUES FOR THE AUGER PARAMETERS AND  $U_{\text{eff}}$  (SEE TEXT)

Surface coverage ( $\sigma$ )	$E_K(\text{Cu}L_3M_{45}M_{45})$	$E_B(\text{Cu}2p_{3/2})$	$E_B(3d)$	Auger parameter	$U_{\text{eff}}$
$6 \times 10^{13}$ atoms $\text{cm}^{-2}$	915.6	933.4	3.9	1849.0	10.0
$\sim 14 \text{ \AA}$ thick Cu layer	918.8	932.8	2.9	1851.6	8.2

smaller than those of Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> (18).  $\Delta G_f(\text{Cu}_2\text{O}) = -146 \text{ kJ mole}^{-1}$ ,  $\Delta G_f(\text{CuO}) = -130 \text{ kJ mole}^{-1}$ ,  $\Delta G_f(\text{TiO}_2, \text{rutile}) = -889 \text{ kJ mole}^{-1}$ ,  $\Delta G_f(\text{Al}_2\text{O}_3) = -1582.4 \text{ kJ mole}^{-1}$ . Therefore the possibility of Cu particles being oxidized under our experimental conditions is thermodynamically unfavorable. Furthermore, oxidation studies of Cu/Al systems, at room temperature (20) have revealed that during the initial stages of oxidation, only Al is oxidized whereas Cu is unaffected.

## 5. Conclusions

It has been shown that a combination of XP and X-ray excited Auger studies can be effectively used to study cluster size and relaxation effects in small Cu clusters supported on model substrates of TiO<sub>2</sub>, graphite, and Al<sub>2</sub>O<sub>3</sub> substrates. Based on the spectral changes, we believe that the greatest dispersion (i.e., smallest clusters) occur with the TiO<sub>2</sub> substrate. Most catalysts are transition metals with unfilled *d*-bands so that the variations in the cluster size can

permit variations in the *d*-band electron density. Consequently, we might expect the catalytic properties of the clusters to vary with their size.

## References

1. M. G. MASON, *Phys. Rev. B* **27**, 151 (1983).
2. P. N. ROSE, K. MINOSHITA, AND P. STONEHART, *J. Catal.* **32**, 163 (1974).
3. F. BOZON-VERDURAZ, A. OMAR, J. ESCARD, AND B. IMELIK, *J. Chem. Soc. Faraday Trans.* **74**, 440 (1978).
4. S. LADAS, R. A. DALLA BETTA, AND M. BOURDART, *J. Catal.* **53**, 356 (1978).
5. T. T. P. CHEUNG, *Surf. Sci.* **140**, 151 (1984).
6. E. ANTONIDES, E. C. JANSE, AND G. A. SAWATZKY, *Phys. Rev. B* **15**, 1669 (1977).
7. S. KOHIKI, *Appl. Surf. Sci.* **25**, 81 (1986).
8. I. JIRKA, *Surf. Sci.* **232**, 307 (1990).
9. M. CINI, *Solid State Commun.* **24**, 681 (1977).
10. G. A. SAWATZKY, *Phys. Rev. Lett.* **39**, 504 (1977).
11. P. T. ANDREWS, T. COLLINS, AND P. WEIGHTMAN, *J. Phys. C. Solid State Phys.* **19**, 435 (1986).
12. C. D. WAGNER, *Faraday Discuss. Chem. Soc.* **60**, 291 (1975).
13. R. W. JOYNER, M. W. ROBERTS, AND K. YATES, *Surf. Sci.* **87**, 501 (1979).
14. A. F. CARLEY AND M. W. ROBERTS, *Proc. R. Soc. London A* **363**, 403 (1978).
15. A. F. CARLEY, Ph.D. thesis, University of Bradford (1980).
16. R. T. K. BAKER, E. R. PRESTRIDE, AND R. L. GARTEN, *J. Catal.* **56**, 390 (1979).
17. M. DE CRESCENZI, M. DI OCIAIUTI, L. LOSSI, P. PICOZZI, S. SANTUCCI, C. BATTISTONI, AND G. MATTOGNO, *Surf. Sci.* **178**, 282 (1986).
18. M. K. BAHL, S. C. TSAI, AND Y. W. CHUNG, *Phys. Rev. B* **15**, 1344 (1980).
19. G. K. WERTHEIM, S. B. DI CENZO AND D. N. E. BUCHANAN, *Phys. Rev. B* **33**, 5384 (1986).
20. M. K. RAJUMON, M. S. HEGDE, AND C. N. R. RAO, *Solid State Commun.* **60**, 267 (1986).

TABLE IV

DIFFERENCE IN THE VALUES OF  $\alpha$ ,  $U_{\text{eff}}$ , AND  $R_{\text{ea}}$  FOR Cu/TiO<sub>2</sub>, Cu/GRAPHITE, AND Cu/Al<sub>2</sub>O<sub>3</sub> AT LOW AND HIGH COVERAGES OF Cu

	$\Delta\alpha^{\text{CS}}$	$\Delta U_{\text{eff}}$	$\Delta R_{\text{ea}}$
Cu/TiO <sub>2</sub>	-3.6	3.4	-0.1
Cu/graphite	-0.8	0	-0.4
Cu/Al <sub>2</sub> O <sub>3</sub>	-2.6	1.8	-0.4