Adsorbate-induced changes in the broadband infrared reflectance of a metal: Oxygen on Cu(100)

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We have measured the adsorbate-induced change in the infrared reflectance of a Cu(100) surface upon adsorption of oxygen at room temperature, at four oxygen coverages, over the frequency range from 100 to 2000 cm\(^{-1}\). The observed frequency dependence provides an independent test of a model of conduction-electron scattering from disordered adsorbates that incorporates nonlocal electrodynamics. We find good agreement with theory for coverages below 0.25 ML. The value of the characteristic roll-off frequency \(\omega_c v_F/c\), however, which is predicted to be independent of the adsorbate, is different from that found for CO on the same crystal. At 0.35-ML coverage, the frequency dependence deviates strongly from the predicted form and the magnitude of the reflectance change decreases. It is possible that these deviations are related to an incipient ordering and reconstruction of the surface.

I. INTRODUCTION

Reflection-absorption infrared spectroscopy, which measures the change in infrared reflectance of a metal surface upon adsorption of a foreign species, has become a standard technique in surface science. Attention is usually focused on the sharp spectral features caused by vibrational resonances of the adsorbed species. The adsorbate, however, can also affect the broadband optical response. The electronic polarizability of the adsorbate itself is expected to have only extremely subtle effects—a slight distortion of the vibrational line shape and a very small (typically \(<0.01\%\)) increase in the broadband reflectance.\(^1\) In a few cases, however, careful measurements have detected much larger (\(\sim1\%\)) adsorbate-induced changes in the broadband reflectance at IR (Refs. 2–10) and visible\(^1\)–\(^3\) frequencies. In these cases the adsorbate is clearly affecting electronic transport in the metal. The reflectance changes have been variously attributed to electronic surface states\(^2\) \(^5\),\(^6\) or to the scattering of conduction electrons by the adsorbate.\(^3\) \(^5\),\(^7\)–\(^9\),\(^11\)–\(^14\)

In this paper we present an investigation of the changes in the broadband IR reflectance of a Cu(100) surface induced by adsorbed oxygen. We provide an independent test of the frequency dependence predicted by Persson and Volokitin\(^1\)\(^5\),\(^6\) based on a model of conduction-electron scattering and nonlocal electrodynamics. We find generally good agreement for coverages below 0.25 ML. At higher coverage we find a marked change in behavior, which we suggest may be associated with an incipient surface reconstruction. There is also an unexplained discrepancy between the roll-off frequency for O on Cu(100) and that previously estimated for CO on the same crystal.

II. EXPERIMENTAL PROCEDURES

The experiments were performed at the U4IR far-infrared beamline at the National Synchrotron Light Source at Brookhaven National Laboratory. Details of the optics have been presented elsewhere.\(^6\) The light was \(p\)-polarized and incident at an angle of 85° to the surface normal; these conditions are nearly optimal for the observation of reflectance changes due either to adsorbate vibrations or to changes in surface electronic properties.\(^1\) Ultrahigh-vacuum-compatible polyethylene windows allowed spectra to be measured at frequencies as low as 50 cm\(^{-1}\), but had low transmittance above 750 cm\(^{-1}\) resulting in noise and gaps in the spectrum. We measured spectra from 100 to 2000 cm\(^{-1}\) using two detectors: a Si:B bolometer for frequencies below 650 cm\(^{-1}\) and a Ge:Cu photodiode for frequencies above 400 cm\(^{-1}\). The nominal resolution was 6 cm\(^{-1}\) for the bolometer data and 16 cm\(^{-1}\) for the photodiode data. During each run the sample temperature was stabilized to avoid thermally induced signal drift (a change in temperature of 5 K produced observable intensity changes). The data presented here represent runs at varied sample temperatures between 300 and 330 K; the results were found to be insensitive to temperature within this range.

The Cu(100) crystal was the same one used in Refs. 6 and 7. It was cleaned by Ne ion bombardment at 550 K followed by annealing between 700 and 850 K. No impurity exhibited an Auger intensity larger than 0.3% of the Cu 920-eV peak. Dosing was accomplished by backfilling the chamber with \(O_2\) gas. At these temperatures \(O_2\) dissociates on the surface leaving an overlayer of atomic oxygen.\(^1\)\(^8\)–\(^25\) Heating and cooling the sample invariably resulted in severe baseline drift, so it was not annealed after dosing. The coverage was determined from
FIG. 1. Ratio of the oxygen KLL to copper LMM Auger intensities as a function of oxygen dosage at 300 K. The coverage scale on the right axis is obtained by assuming a saturation coverage of 0.50 ML. The solid symbols are our measurements on two separate days; the open circles show coverage vs exposure data from Ref. 20. The inset shows an enlargement of the low-dosage region.

the oxygen dosage using Fig. 1, which shows our data for the ratio of the oxygen KLL Auger intensity (512 eV) to the Cu LMM intensity (920 eV) as a function of dosage at 300 K. The coverage scale is determined by assuming \( \theta = 0.5 \) ML at saturation.\(^{20}\) For comparison, Fig. 1 also shows the corresponding coverage vs exposure data of Wuttig, Franchy, and Ibach.\(^{20}\)

We also conducted qualitative low-energy electron-diffraction (LEED) observations. At the coverages and temperatures discussed here, no overlayer ordering was observed, consistent with other reports\(^{20-25}\) that annealing is required for optimum ordering. At higher coverages (> 0.45 ML) we did observe a \( c(2 \times 2) \) pattern, which according to Wuttig, Franchy, and Ibach\(^{20}\) is in fact characteristic of the \( (2\sqrt{2} \times 2) R45^\circ \) reconstructed phase.

III. DATA REDUCTION AND RESULTS

The intensity of synchrotron radiation is proportional to the current in the stored electron beam,\(^{26}\) and all spectra were normalized to the beam current before analysis. Uncertainties in the current and drift of the stored electron beam, however, can cause intensity variations that mimic reflectance changes. To exclude such spurious effects we adopted a stringent and unbiased system of data selection and analysis, as described in the following three paragraphs.

After the sample had been cleaned and its temperature was stable, four to eight consecutive reference spectra were measured. Each spectrum comprised 128 scans and took 55 sec. The sample was dosed with oxygen and another set of spectra was measured. Ratios of the individual, current-normalized reference spectra with each other were examined, as well as ratios among the individual post-dosing spectra. If any of these ratios of nominally identical spectra showed baseline deviations greater than 0.2% between 300 and 2000 cm\(^{-1}\), the entire experiment was discarded. Comparisons of the post-dosing spectra with the reference spectra were not used in selecting the data. Approximately one-third of the experiments met the stability criterion, leaving three photoconductor and two bolometer runs for \( \theta = 0.25 \) ML and one run with each detector at 0.08-, 0.17-, and 0.35-ML coverage. Because of the long doses required, spectra at higher coverages invariably showed excessive drift.

The reference and post-dosing spectra from each run were averaged, and the fractional reflectance change

FIG. 2. Oxygen-induced fractional reflectance change \( \Delta R/R \) for four oxygen coverages: (a) 0.08 ML; (b) 0.17 ML; (c) 0.25 ML; (d) 0.35 ML. The gaps in the spectra and the noise at high frequencies are due to the low transmittance of the polyethylene windows. The solid lines are fits to Eq. (2) as discussed in the text; for spectrum (d) no fit was possible.
\( \Delta R / R \) was calculated. Owing to systematic errors, there was in general an offset (typically \( \sim 0.05\% \)) between the bolometer and photoconductor spectra in the frequency range \((400-650\ \text{cm}^{-1})\) covered by both detectors. To obtain a final composite spectrum the bolometer data were offset to agree with the photoconductor signal. For \( \theta = 0.08 \) and 0.35 ML, baseline deviations were found below 300 cm\(^{-1} \) and the low-frequency region was discarded.

As a final check against instrumental drift, the oxygen dosage was increased (if necessary) to 50 L (1 L = \( 1 \times 10^{-6} \) torr sec) and the sample was exposed to 50 L of formic acid, which removed the adsorbed oxygen, leaving behind a layer of surface formate.\(^{27} \) The reflectance change \( \Delta R / R \) (relative to the clean surface) returned to zero within 0.2%, clearly demonstrating that the reflectance changes shown are in fact oxygen induced. For oxygen coverages > 0.25 ML formic acid does not completely remove the oxygen, and this test could not be used.

Figure 2 presents composite reflectance spectra for four coverages of O on Cu(100). All show the same qualitative behavior—the reflectance change is negative, and its magnitude is small at low frequencies, increases rapidly between 200 and 600 cm\(^{-1} \), and reaches an asymptotic value above 1500 cm\(^{-1} \). Theoretical considerations require \( \Delta R / R \) to approach zero at zero frequency, as the wavelength and penetration depth of the field become infinite.\(^{14-16} \) We therefore attribute the apparent nonzero intercepts to systematic errors. The lines in Figs. 2(a)–2(c) are discussed in Sec. IV.

Cu-O stretching vibrations are expected near 340 cm\(^{-1} \) at low coverage and near 290 cm\(^{-1} \) at higher coverage.\(^{19,20,28} \) We were unable to observe these modes, despite a sensitivity to reflectance changes of 0.02%. In Sec. VI we use this information to place an upper limit to the dynamic dipole moment of the vibration, and compare it with other experimental and theoretical results.

**IV. FREQUENCY DEPENDENCE**

In a series of papers, Persson and Volokitin\(^ {14-16} \) have elaborated a model of adsorbate-induced reflectance changes, based on diffuse scattering of conduction electrons by disordered adsorbates. The most general form, valid for free electron metals at IR frequencies \( \omega >> \tau^{-1} \) [\( \tau \) is the bulk scattering time; for Cu \( \tau^{-1} \) corresponds to a frequency of \( \sim 75 \ \text{cm}^{-1} \) (Ref. 7)], is\(^ {16} \)

\[
\frac{\Delta R}{R} = -\frac{4a}{\pi^2} \left( \frac{\omega}{\omega_1} \right)^2 \Re \left[ g \left( \omega / \omega_1, l / \delta \right) \right] 
- \frac{4\omega}{\pi \omega_p \cos \theta} \int_{-\infty}^{\infty} dq \left( \omega / \omega_1, l / \delta, q \right)
\]

(1)

where \( g(x,z) \) and \( \epsilon(x,z,q) \) are complex-valued functions defined in Ref. 16, \( l \) is the electron mean-free path, \( \omega_p \) is the plasma frequency of the metal, \( \delta = c / \omega_p \) is the classical skin depth, and \( \omega_1 = \omega_p \sqrt{\epsilon / c} \) is a characteristic roll-off frequency, near and below which nonlocal effects become important.

Applying Eq. (1) to the data of Hirschmugl et al.\(^ {6} \) for CO on Cu(100), Persson found a good fit with a value of \( \omega_1 = 500 \ \text{cm}^{-1} \), on the same order as theoretical estimates of 310 (Ref. 7) and 444 cm\(^{-1} \).\(^ {15,16} \) An analysis of newer data found a value of 400 cm\(^{-1} \). The theoretical predictions tested here is that only the magnitude \( a \) should depend upon the adsorbate or the coverage; the spectral shape and the parameter \( \omega_1 \) should be properties only of the substrate.

Equation (1) is computationally very cumbersome, and we did not attempt to fit it systematically to our data. Over the frequency range studied here, it is extremely well approximated by a much simpler expression,

\[
\frac{\Delta R}{R} = C - a \frac{\omega^2}{\omega^2 + \tilde{\omega}^2},
\]

(2)

where for \( l / \delta = 4.2 \), appropriate for Cu at room temperature,\(^ {7} \) the parameters in Eqs. (1) and (2) are related by

\[
C = -0.00064a,
\]

\[
\tilde{\omega} = 0.96a,
\]

\[
\tilde{\omega} = 1.21a_1.
\]

Note that Eq. (2) is very similar to the approximation proposed by Persson\(^ {15} \) building on the work of Dingle.\(^ {29} \)

We have performed weighted least-squares fits of Eq. (2) to our data, including an additional adjustable offset \( C' \) to account for systematic errors in the current normalization. The solid lines in Figs. 2(a)–2(c) show the results, and Table I gives the values and uncertainties of the parameters \( a \) and \( \omega_1 \) in Eq. (1) [obtained through Eqs. (3)] and of the instrumental offset \( (C' - C) \), for each coverage at which a fit was possible. The uncertainties were estimated by examining the \( \chi^2 \) contours near the minimum, and for normally distributed errors represent better than 99% confidence limits. Also given are the values of \( \chi^2 \), which indicate\(^ {30} \) an excellent fit for the two lowest coverages (0.08 and 0.17 ML). The fit to the 0.25-ML coverage data is still good, but there is a small but significant discrepancy in the 800–1200-cm\(^{-1} \) region.

Figure 3 compares Eq. (2) (solid line) with Eq. (1), using parameters related through Eqs. (3), for our data for \( \theta = 0.25 \ \text{ML} \) with \( C' \) subtracted. Within the accuracy of our measurements, the two curves are indistinguishable. Some disagreement is apparent at very low frequencies, where the general theory [Eq. (1)] predicts that the reflectance change goes to zero with nonzero slope but near-zero curvature. The data, on the other hand, seem to be approaching zero slope with a distinct negative curvature—similar to the behavior of the approximate expression [Eq. (2)]. A similar trend is visible in the data for CO.\(^ {6,15,16} \) While the discrepancies are too small to be conclusive, they may hint at an incompleteness in the theory at very low frequencies, and suggest the need for further theoretical work.

For the three lowest coverages the excellent agreement of Eqs. (1) and (2) with the data provides strong support for the model of Persson and Volokitin. The values of \( \omega_1 \) for the three coverages are also consistent. (The large uncertainty in \( \omega_1 \) for \( \theta = 0.08 \ \text{ML} \) is caused by the weak variation of the reflectance and by the absence of data at low frequencies.) Assuming that \( \omega_1 \) is independent of
TABLE I. Best-fit parameter values and $\chi^2$ obtained by fitting Eq. (2) to the spectra in Figs. 2(a)–2(c), and transforming the fitting parameters according to Eqs. (3). Figure 2(d) could not be fit with Eq. (2). The determination of the uncertainties is discussed in the text. The weighted average of the $\omega_1$ values is $338 \pm 34$ cm$^{-1}$. Also listed are the values of $a$ and $\omega_1 = \omega_{v_F}/c$ found for CO on the same Cu(100) crystal, and the value of $\omega_1$ predicted from a free-electron model of Cu (Refs. 7 and 15).

<table>
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<th>O/Cu(100) coverage</th>
<th>$a$ (%)</th>
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<td>$-0.47^{+0.13}_{-0.08}$</td>
<td>$555^{+75}_{-71}$</td>
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<td>1.06</td>
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<tr>
<td>0.17</td>
<td>$-0.63^{+0.08}_{-0.05}$</td>
<td>$331^{+72}_{-71}$</td>
<td>$-0.16^{+0.04}_{-0.05}$</td>
<td>1.10</td>
</tr>
<tr>
<td>0.25</td>
<td>$-0.14^{+0.08}_{-0.05}$</td>
<td>$339^{+72}_{-71}$</td>
<td>$-0.23^{+0.04}_{-0.05}$</td>
<td>1.34</td>
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<tr>
<td>CO/Cu(100)</td>
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<td>0.4$^a$</td>
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<td>0.5$^b$</td>
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</table>

$^a$References 6 and 16.
$^b$Reference 8.
$^c$Reference 15, based on one electron per Cu atom.
$^d$Reference 7, based on an electron density deduced from optical measurements.

covariance—as predicted by the theory—the weighted average for the three curves gives $\omega_1 = 338 \pm 34$ cm$^{-1}$. It is surprising that this estimate differs from the values of 500 (Ref. 16) and 400 cm$^{-1}$ (Ref. 8) found for CO on exactly the same Cu(100) crystal, since $\omega_1 = \omega_{v_F}/c$ should be independent of the adsorbate and the temperature.

The high-coverage (0.35 ML) data could not be fit by Eq. (2) (the minimum value of $\chi^2$ was 10.2). Since the form of the frequency dependence depends only on the assumption that the dominant effect of the adsorbate on conduction is increased scattering, this deviation suggests that other processes may be important at high coverages.

Within the scattering model, the magnitude $a$ of the asymptotic reflectance change at high frequencies ($\omega \gg \omega_1$) is related to the change in dc resistivity $\Delta \rho$ of a thin film of the same metal according to $^7$,

$$ a = \frac{4ne^2}{mc} \frac{1}{\cos \theta} \left[ t \Delta \rho(t) \right], $$

where $n$ is the conduction electron density, $m$ is the effective mass, $t$ is the thickness of the thin film, and $\theta$ is the angle of incidence. The quantity $t \Delta \rho$ is independent of $t$ for a given adsorption system. $^{31,32}$

In an earlier publication $^7$ we compared the reflectance change at high frequency ($> 1500$ cm$^{-1}$) for single coverages of oxygen and CO on Cu(100) and of CO on Ni(100) with the value predicted from Eq. (4), using published data for the resistivity change of thin films. $^{33-35}$

Given the large variations and uncertainties in the resistivity data, and in the comparison between measurements on dissimilar samples, the agreement was reasonably good for the adsorbates on Cu. For CO on Ni(100), however, the predicted reflectance change was large ($\sim 6\%$) while essentially no reflectance change ($< 0.4\%$) was found experimentally; $^7$ Persson and Volokitin $^{16}$ have offered a qualitative explanation that can account for roughly a factor of 2 difference between the predicted and measured values, but does not explain the factor of 30 difference that was observed. The present work provides a much more exacting test of the scattering model by focusing attention on the frequency dependence of the reflectance change, which avoids the large uncertainties in the resistivity data. In the next section we also examine the dependence of the reflectance change on coverage.

V. COVERAGE DEPENDENCE

An important consequence of the scattering model is a qualitative prediction of the dependence of the reflectance or resistivity change on adsorbate coverage. At low coverage the adsorbates are randomly distributed, in the absence of long-range interactions, and the resistivity or reflectance change should vary linearly with the coverage. At higher coverage, the adsorbates may form an ordered overlayer. The effect of ordering on the resis-

![Graph](image_url)
tivity and reflectance is an unsettled issue both theoretically and experimentally. No diffuse scattering is possible from an ordered surface, but Bragg scattering will contribute to the resistivity if the unit cell of the overlayer is larger than that of the clean surface. We would expect the Bragg scattering contribution to be less than that from diffuse scattering from the same adsorbate coverage, so that ordering should produce a decrease in the resistivity and in the magnitude of the reflectance change.

Resistivity measurements on thin films sometimes exhibit a maximum as a function of adsorbate coverage, but the resistance does not approach the clean-surface value and there is no direct evidence associating the decrease in resistance at high coverage with ordering. An IR reflectance study of H on W(100) by Riffe and Sievers found a decrease in the magnitude of the reflectance change upon ordering, as expected. For CO on Cu(100), however, Hirschmuller et al. observed a linear increase with no detectable change in slope as the ordered (2×2) structure formed.

Figure 4 presents our data for the asymptotic (high-frequency) magnitude of the fractional reflectance change as a function of coverage. For the three lowest coverages, the values and uncertainties are those listed in Table I for the parameter α. For θ=0.35 ML we have made an estimate from the high-frequency portion of Fig. 2(d). The uncertainty in the coverage includes both errors in dosing and uncertainty in the coverage vs dosage curve (Fig. 1).

A qualitative change in behavior at the highest coverage is apparent both from Fig. 4 and from Fig. 2; the magnitude of the reflectance change, rather than continuing to increase, drops about 20% from its value at 0.25 ML coverage. At the same time, the shape of the frequency dependence undergoes a marked change, reflected in the inability to fit the 0.35-ML coverage data, even approximately, with Eq. (2). While the information is certainly incomplete, we suggest that this change of behavior is related to the tendency of oxygen on Cu(100) to form an ordered, reconstructed surface at a coverage close to 0.35 ML. A number of experiments have established the existence of a (2√2×√2)R45° structure involving a “missing row” reconstruction: every fourth row of Cu atoms is vacant. According to the LEED study of Wuttig, Franchy, and Ibach, 20 there is a first-order phase transition from a disordered layer into the ordered phase at a critical coverage θe=0.34 ML, close to the highest coverage we were able to study.

Our own LEED observations did not reveal the (2√2×√2)R45° pattern at the coverages studied, probably because we were not able to anneal the overlayer (heating and cooling the sample invariably resulted in spurious baseline shifts). Equilibration of the overlayer and formation of the ordered phase are known to require annealing to at least 400 K. 20-25 It is possible, nonetheless, that some partial or local ordering was occurring at room temperature, which could not be observed with LEED but had a noticeable effect on the reflectance change. Qualitatively, we would expect some reduction in diffuse scattering for ordering on a length scale greater than the electrons' Fermi wavelength, approximately 5 Å for Cu; it is therefore plausible that ordering on a length scale too short to be observed with LEED could have an observable effect on the reflectance. We present this possibility as a speculation; clearly additional experiments are needed for a definitive conclusion.

We also display in Fig. 4 the coverage dependence of the resistivity change observed for oxygen on a thin copper film. The three lowest coverage points behave similarly to the resistivity, with the reflectance change increasing monotonically, but with decreasing slope. The drop in the magnitude of the reflectance change at 0.35 ML coverage, however, is not mirrored in the resistivity curve. The resistivity curve does exhibit a smaller (~10%) drop at a higher coverage (>0.6 ML, not shown in Fig. 4). If the drops are associated with surface ordering, it is not surprising that the two curves are different, since the surfaces are dissimilar (the films are heterogeneous, but expected to be predominantly of [111] orientation). Alternatively, it is possible that the actual adsorbate coverages in the resistivity experiments were substantially lower than estimated.

VI. DYNAMIC DIPOLE MOMENT

We did not observe a convincing Cu-O stretch signal, despite a sensitivity of 0.02%. Using an estimated linewidth of 50 cm⁻¹ (Ref. 20) we find that the dynamic dipole moment e*<0.12e. This compares with values from 0.12e to 0.18e estimated from electron-energy-loss spectroscopy (EELS) intensities, assuming typical values of 1°-1.5° for the spectrometer acceptance half-angle. Possibly the lines were broadened in our experiment because the sample was not annealed, or part of the EELS intensity may result from impact scattering.

The e* value for the Cu-O mode is rather small compared even to other adsorbate-substrate vibrations. This may be understood qualitatively in terms of screening of the incident electric field by the copper conduction electrons. Structural studies have found that the oxygen is less than 0.25 Å above the center of the top Cu layer, a position which according to jellium calcul-
tions\textsuperscript{29} places it well inside the screening electron density. Theoretical calculations of $e^*$ that include the effects of screening, however, give much larger values, in the vicinity of $e^* = 1.0 \times 10^{40,41}$ This large discrepancy merits further theoretical investigation.

\section*{VII. CONCLUSION}

We have measured the adsorbate-induced change in infrared reflectance over a wide frequency range (100–2000 cm$^{-1}$) for oxygen on Cu(100) near room temperature. Our data offer a test of a proposed model of surface scattering that incorporates nonlocal electromagnetics.\textsuperscript{15,16} For coverages below 0.25 ML, the data strongly support the model. A qualitative change in behavior is observed at the highest coverage studied (0.35 ML), where the magnitude of the reflectance change drops and the shape of the frequency dependence changes markedly. We speculate that these changes may be associated with an incipient phase transition into the $(2\sqrt{2} \times \sqrt{2})R45^\circ$ ordered phase, although we were not able to anneal the surface to obtain long-range ordering.

\section*{ACKNOWLEDGMENTS}

This research was carried out (in part) at the National Synchrotron Light Source, Brookhaven National Laboratory, which is supported by the U.S. Department of Energy, Division of Materials Sciences and Division of Chemical Sciences. K.C.L. and R.G.T. acknowledge the support of the NSF under Grant Nos. DMR-8815616 and DMR-9201077. This work forms part of a collaboration between P.D. and G. P. Williams under International Collaborative Award No. INT-9016771, funded by the NSF and CNRS (France). We thank C. J. Hirschmugl and G. P. Williams for their hospitality and assistance at Brookhaven National Laboratory, and B. N. J. Persson for providing results prior to publication.

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\textsuperscript{40}N. D. Lang and W. Kohn, Phys. Rev. B 7, 3541 (1973).


(3.6) and (C5) should be replaced by

$$\frac{\omega_b}{W} = -3 \left( \frac{\pi}{4} \left[ 1 + \frac{1}{S} \right] \right)^{2/3} \left( \frac{IS}{W} \right)^{4/3}.$$  \hspace{1cm} (3.6) and (C5)

These corrections do not change the results at the high-temperature limit, although there are some quantitative changes in the results for the paramagnetic temperatures (Figs. 8-13): These corrections lower the energy of the bottom of the band at the paramagnetic temperatures further than that previously reported, which is shown here in Figs. 9 and 10.

Erratum: Adsorbate-induced changes in the broadband infrared reflectance of a metal: Oxygen on Cu(100)


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There are several misprints in Table I. The table should read as follows.

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$^a$References 6 and 16.
$^b$Reference 8.
$^c$Reference 15, based on one electron per Cu atom.
$^d$Reference 7, based on an electron density deduced from optical measurements.

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