

Effect of Ag on the surface barrier for depletion of oxygen from polycrystalline $\text{YBa}_2\text{Cu}_3\text{O}_7$ oxides

A. G. Schrott, K. N. Tu, N. C. Yeh, G. Singco, A. Levi, and C. C. Tsuei

IBM Research Division, Thomas J. Watson Research Center, Yorktown Heights, New York 10598

(Received 19 September 1988; revised manuscript received 14 November 1988)

We have investigated the effect of evaporated Ag on the depletion of oxygen from polycrystalline $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ in a He ambient atmosphere by *in situ* resistivity experiments and surface spectroscopies. Our data indicate an increase in the rate of out-diffusion of oxygen due to the presence of the Ag, which lowers the surface barrier for the out-diffusion of oxygen by 0.2 ± 0.03 eV. We have performed x-ray photoelectron spectroscopy (XPS) analysis of the *in situ* fractured surfaces to indicate the presence of Ag at the internal surfaces in the oxide. XPS data from Ag-free *in situ* scraped samples show oxygen accumulation in the near-surface region upon vacuum annealing. This effect is prevented by evaporation of a few monolayers of Ag. Changes in the cutoff energies of the ultraviolet photoelectron spectra indicate that a submonolayer coverage of Ag is sufficient to produce a change in the work function of 0.3 eV, corresponding to the lowering of the surface barrier.

The surface composition and structure of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is a subject of considerable interest not only in itself, but also for its importance to grain boundary properties of the superconducting ceramics. Tu and co-workers^{1,2} have measured the rate of out-diffusion (and in-diffusion) of oxygen in polycrystalline samples and found that the out-diffusion is surface reaction limited with an activation energy of 1.7 ± 0.1 eV. This surface barrier for oxygen out-diffusion may have an important influence on grain boundary properties, in view of the annealing cycles that are typically performed on ceramic samples to obtain the highest critical temperature T_c . This procedure may change the composition of the grain boundaries, and in turn, the critical current density J_c . In this Rapid Communication, we report our study of the effect of Ag on modifying the surface barrier. We have observed a lowering of the barrier of oxygen out-diffusion by depositing and annealing of Ag film on $\text{YBa}_2\text{Cu}_3\text{O}_7$ oxides. We have used x-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) to assess possible chemical and compositional changes occurring in the surface region upon oxygen out-diffusion, and also to assess the effect of evaporated Ag on surface bonding.

The experimental procedure regarding sample preparation and *in situ* resistivity measurements for monitoring the oxygen out-diffusion have been reported elsewhere.¹ We took two identical pieces ($5 \times 3 \times 1$ mm³) cut from a sintered bulk ceramic sample. One of the pieces was coated (*ex situ*) on all the external surfaces with about 500-Å Ag and then annealed in O_2 for 20 h at 750°C. For comparison, similar *in situ* resistivity measurements and surface analysis were performed on these two pieces. The photoemission experiments were performed in a VG ESCA-lab MK II. Ag was also evaporated *in situ* on clean $\text{YBa}_2\text{Cu}_3\text{O}_7$ surfaces at a base pressure of $\approx 10^{-10}$ mbar, and the film thickness was measured by a crystal quartz monitor calibrated with Rutherford backscattering (RBS). We examined the surfaces of *in situ* fractured and *in situ* scraped samples by XPS and UPS. The *in situ* fracture was performed on the pieces described above,

leaving the cross section (3×1 mm²) available for the photoemission measurements. Prior to the *in situ* fracture, the samples were coated with C to prevent detection of signals from the side surfaces. When the sample was scraped *in vacuo*, it was simultaneously cooled to 160 K in order to prevent undesired sample heating during scraping. The spectra from freshly scraped samples were taken at 160 K and were considered representative of the bulk structure of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. This procedure minimizes the contribution to the signals from grain boundary phases [e.g., BaCO_3 (Ref. 3)] and is generally accepted as adequate.³⁻⁷

The solid curve in Fig. 1 shows the resistivity change of the polycrystalline $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ($\delta \approx 0$) sample upon heating in He from room temperature to 520°C. The controlled heating rate was 0.5°C/min. The dashed curve in Fig. 1 shows the resistivity change, at the same heating rate, of the companion $\text{YBa}_2\text{Cu}_3\text{O}_7$ sample that was coated with Ag. We note that in the Ag-coated sample, oxygen departs from the sample at a faster rate than the uncoated sample. The departure of the resistivity curve from the linear temperature dependence is indicative of oxygen out-diffusion, and, therefore, can be utilized to obtain the out-diffusion activation energy, as discussed in Ref. 2. The inset in Fig. 1 shows the activation energies of the surface barrier extracted from curves *a* and *b*, respectively.^{1,2} We found that the activation energy corresponding to the sample treated with Ag is 0.2 eV lower than the value for the uncoated sample. Two pairs of these samples have been studied and the results are the same. We measured T_c of these samples by the resistivity versus temperature technique before and after the treatment with Ag and temperature cycling. In both cases, T_c (zero resistance value) was 91.5 K and the transition width was ≈ 1 K. We have also estimated J_c at 6 K using a superconducting quantum interference device (SQUID) magnetometer and the Bean formula. We found that the initial value of $\approx 5 \times 10^4$ A/cm² did not change, within experimental error, after the Ag treatment and temperature cycling. These T_c and J_c measurements suggest no detri-

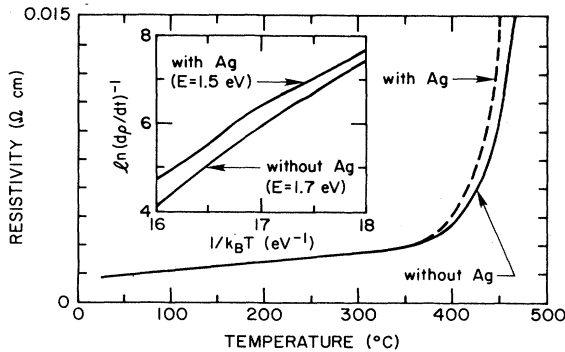


FIG. 1. The solid and dashed curves show the resistivity change of $\text{YBa}_2\text{Cu}_3\text{O}_7$ ceramic oxide samples without and with Ag, respectively, upon annealing in He ambient at a heating rate of $0.5^\circ\text{C}/\text{min}$. The inset shows the corresponding plots of $\ln(dp/dt)^{-1}$ vs $1/k_B T$, where the slope of the curves gives an activation energy of 1.7 and 1.5 eV, respectively.

mental interaction of Ag with the bulk of $\text{YBa}_2\text{Cu}_3\text{O}_7$.

A scanning-electron-microscopy (SEM) investigation of the fractured surfaces showed no significant differences between the samples with and without Ag. Direct evidence for the presence of Ag in the corresponding samples was obtained by XPS analysis of the *in situ* fractured surfaces, performed after the resistivity measurements. Since these XPS spectra may have contributions from possible grain-boundary phases,³ they were not used to assess the effects of Ag on surface bonding. The intensity of the Ag $3d$ XPS peak, relative to those of the substrate, was about half of that measured upon evaporation of 0.5 \AA of Ag on a clean $\text{YBa}_2\text{Cu}_3\text{O}_7$ surface. This implies a Ag atomic surface concentration of the order of 0.1. However, if all the Ag atoms were dissolved uniformly into the bulk, we should expect an atomic concentration of about 10^{-4} , and this would be below the standard detectability limits of XPS. Since the typical percentage of intergranular fracture for $\text{YBa}_2\text{Cu}_3\text{O}_7$ is about 50%,³ the XPS results indicate that Ag diffuses into the internal surfaces and the grain boundaries, rather than dissolves into the grains of the oxide. This conclusion is supported by the observation of a decrement of the relative intensity of the Ag lines as the above sample was scraped *in situ*, considering that the effect of scraping is to expose more bulk material.³ Spurious scraping effects, such as segregation due to sample heating, are minimized with our experimental arrangement and have not been observed.

We have shown so far a correlation between the presence of Ag at the internal surfaces of $\text{YBa}_2\text{Cu}_3\text{O}_7$ and a decrease of the surface barrier for oxygen out-diffusion. These results suggest the occurrence of distinct changes occurring at the near-surface region (and possibly at the grain boundaries) due to the oxygen out-diffusion and to the presence of Ag, to be discussed in the next section.

To assess the effects of oxygen out-diffusion on surface bonding, we have examined with photoemission the three kinds of surfaces of polycrystalline $\text{YBa}_2\text{Cu}_3\text{O}_7$ ceramic samples obtained under the following conditions: type (a), after scraping in vacuum the as-received sample

($\delta \approx 0$); type (b), after annealing the scraped samples in vacuum ($\delta \geq 0$); type (c), after scraping once again the vacuum annealed sample ($\delta > 0$).

Figure 2(a) shows the Cu $2p_{3/2}$ XPS spectra for the three $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ surfaces. The Cu $2p$ line shape for $\text{YBa}_2\text{Cu}_3\text{O}_7$ has been compared to those of pure divalent compounds such as CuO (Ref. 6, 8, and 9) or CuCl_2 .^{5,10} In these compounds, the higher (satellites) and lower-binding-energy (main) peaks are associated to $|2p\ 3d^9\rangle$ and $|2p\ 3d^{10}\underline{L}\rangle$ final-state configurations, where $2p(\underline{L})$ denotes a $2p$ (ligand) hole.¹⁰ In searching for the ground state in the electron configuration for Cu in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, no firm evidence of a $|2p\ 3d^8\rangle$ (i.e., Cu^{3+}) state has emerged.^{5,6,9,11,12} Gourieux *et al.*¹³ on the basis of x-ray absorption¹² and Hall-effect studies,¹⁴ postulate a mixture of $|3d^9\rangle$, $|3d^9\underline{L}k\rangle$, and $|3d^{10}\underline{L}\rangle$ states for the ground-state configuration, where k is a conduction electron. Based on Ref. 13, we may assign the Cu $2p_{3/2}$ spectra in Fig. 2 as follows.

The main peak is associated with the well-screened $|2p\ 3d^{10}\underline{L}\rangle$ and $|2p\ 3d^{10}\underline{L}^2k\rangle$ final states, which are separated by $\approx 2 \text{ eV}$, the latter having higher binding energy; the satellites are associated with the poorly screened $|2p\ 3d^9\rangle$ and $|2p\ 3d^9\underline{L}k\rangle$ contributions.

Curve *a* in Fig. 2(a), for a scraped sample in the as-

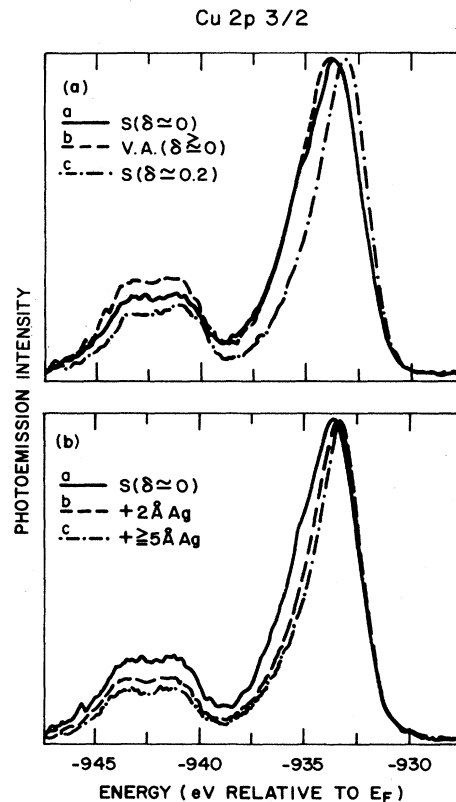


FIG. 2. Cu $2p_{3/2}$ XPS spectra (linear background subtracted) for various $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ surfaces. (a) curve *a*, scraped sample (S), $\delta \approx 0$; curve *b*, vacuum annealed sample (VA), $\delta \geq 0$; curve *c*, scraped sample, $\delta \approx 0.2$. (b) curve *a*, same as in (a); curve *b*, sample in curve *a* + 2-\AA Ag; curve *c*, sample in curve *a* + 5-\AA Ag.

received state ($\delta=0$), exhibits a broad and asymmetric main peak, and a relative satellite intensity lower than that of CuO. Thus, it agrees with previous work.^{5-9,13} In contrast, curve *b* in Fig. 2(a), corresponding to the sample of curve *a* after it was heated for 1 h at 350°C in vacuum ($P \approx 5 \times 10^{-11}$ mbar) shows an increase in the high-binding-energy shoulder of the main peak, and a higher relative intensity of the satellites. These changes in the Cu 2*p* line shape are accompanied by a small shift (0.2 eV) in the O 1*s* XPS line (not shown) to higher binding energies, as well as by a larger O 1*s*-Cu 2*p* intensity ratio than that for curve *a*, and are consistent with a higher proportion of $|3d^9\bar{L}k\rangle$ in the ground state.¹³ Because of the complicated multiplet structure of the satellites and the fact that the $|2p\ 3d^{10}\bar{L}\rangle$ final-state component may originate from either the $|3d^9\rangle$ or the $|3d^{10}\bar{L}\rangle$ ground-state contribution, a determination of the relative changes of all three ground-state components would not be reliable. The changes described above can be attributed to accumulation of oxygen near the surface of the oxide. Since the annealing temperature (350°C) is lower than the onset of fast-oxygen out-diffusion,^{1,2} and since the out-diffusion is surface reaction limited,^{1,2} some accumulation of oxygen near the surface of the sample of type (b) can be expected. This should result in stronger oxidation for the Cu valence and therefore could result in an enhancement of the $|3d^9\bar{L}k\rangle$ contribution to the ground state (the equivalent of Cu³⁺) to maintain charge neutrality. Curve *b* is also representative of samples of type (b) that have been annealed at temperatures higher than 350°C where a bulk oxygen deficiency is expected. On the other hand, for a scraped [type (c)] bulk-deficient sample, such as that of curve *c* in Fig. 2(a), which corresponds to an O concentration of ≈ 6.8 ($\delta \approx 0.2$), the XPS spectrum shows a narrower main peak with a downshift of ≈ 0.75 eV and a relatively lower satellite intensity. Notice that within the satellite peak, the intensity of the lower energy portion increases relative to the higher-energy portion. This satellite line shape is typically observed in CuO,^{6,8,9} and it is consistent with the narrower main peak and with a smaller $|3d^9\bar{L}k\rangle$ ground-state component¹³ in the O-deficient sample.

In order to assess the effect of Ag on surface bonding, we evaporated *in situ* very thin layers of Ag onto freshly scraped YBa₂Cu₃O₇ samples. Figure 2(b) shows the evolution of the Cu 2*p*_{3/2} for increasing Ag coverages. We notice a gradual shift towards lower binding energies as the peak width decreases. The satellite intensity also decreases, although its line shape remains similar to that of the clean scraped surface. We measured the decrement of the Cu 2*p* integrated intensity as a function of the monitored Ag thickness and found that it was linear up to ≈ 5 Å, followed by a lower, nonlinear rate. We also observed that the Cu 2*p*_{3/2} line shape did not exhibit further changes beyond that point. Thus, we believe that a fairly good surface coverage of Ag is attained after evaporation of about 5 Å. The remaining relative intensity of the satellites in curve *c* of Fig. 2(b) is consistent with the satellite signal arising from the second and inner layers of Cu atoms (≈ 4 -Å separation),¹⁵ and with an electron mean free path of 8-10 Å.¹⁶ Thus, the changes in Fig. 2(b)

from curves *a* to *c* can be interpreted as the result of a lower oxidation state of the surface copper atoms, yielding an initial state generated mostly by the $|3d^{10}\bar{L}\rangle$ contribution (Cu⁺).

We did not find in the Ag coated surfaces, in contrast to the case of the clean YBa₂Cu₃O₇ surfaces discussed before, changes in either the Cu signal or accumulation of oxygen in the near-surface region upon annealing in vacuum at $T \leq 350$ °C. These XPS signals are consistent with the resistivity measurements that indicate a lower activation energy for oxygen out diffusion.

Additional information is provided by the UPS spectra of Ag evaporated surfaces. Figure 3 shows the UPS (He II, $h\nu = 40.8$ eV) spectra of clean YBa₂Cu₃O₇ surface and those of the same surface after Ag evaporation. In general, the intensity at the Fermi level is not destroyed by the interaction with Ag, in agreement with previous work using synchrotron radiation.¹⁷ However, we interpret the following changes as derived from an Ag-surface interaction, in agreement with our XPS data. Curve *a*, corresponding to the clean sample, reflects mainly the Cu-O character of the density of states in the valence band. The peak at ≈ 2.5 eV is associated with the O density of states, while the peak at ≈ 4.5 eV is believed to be associated with the Cu density of states. Additional features of the UPS spectra are discussed else-

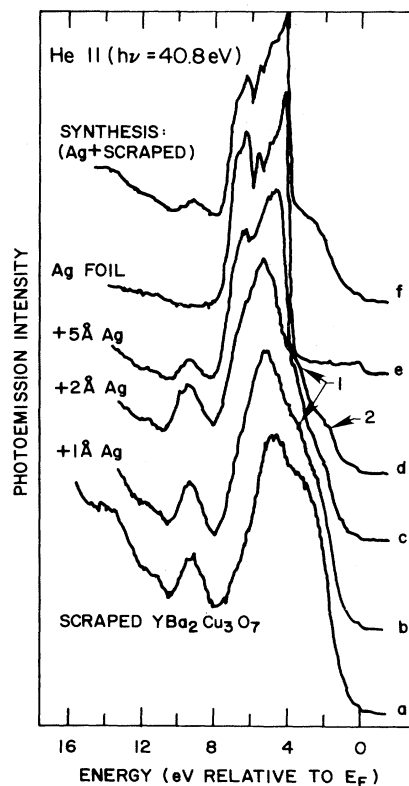


FIG. 3. UPS spectra ($h\nu = 40.8$ eV) for the following surfaces: sample *a*, scraped YBa₂Cu₃O₇; sample *b*, +1-Å Ag; sample *c*, +2-Å Ag; sample *d*, +5-Å Ag; sample *e*, Ag film; sample *f*, 50/50 synthesis of samples *a* and *d*.

where.^{3,4,7,13,18} Curve *b* indicates that $\approx 1 \text{ \AA}$ of Ag produces a significant decrease in the shoulder at 2–3 eV, a shift in the main feature at $\approx 4.5 \text{ eV}$, and the appearance of a new feature (feature 1) at $\approx 3.2 \text{ eV}$. The spectra for 2 and 5 \AA (curves *c* and *d*) also show a feature at $\approx 2 \text{ eV}$ (feature 2). Curve *c* also shows features characteristic of Ag films (curve *e*). Features 1 and 2 have been reported for atomic oxygen chemisorbed on Ag films^{19–21} and are believed to be of O character, while the feature at 5.2 eV is most likely of Ag character.^{19,20} The feature at $\approx 3.2 \text{ eV}$ could also be produced by a Cu 3*d* contribution from Cu⁺ (at $\approx 3 \text{ eV}$ for Cu₂O).²² However, feature 2 is too low in energy to be accounted for a Cu⁰ contribution.²³ Thus, there is no evidence for a direct substitution of the surface Cu by Ag at room temperature. A synthesis of curves *a* and *e*, shown in curve *f*, indicates that the above features do not arise from direct superposition of clean YBa₂Cu₃O₇ and Ag spectra.

We also measured the cutoff energies (using He I, $h\nu = 21.2 \text{ eV}$, not shown in Fig. 3) for the samples of curves *a–e*, and noticed a decrease in the work function of $\approx 0.3 \text{ eV}$ in going from *a* to *b*. This shift in the work function agrees with the observed decrease in the activation energy for O out-diffusion and reflects a distinct bonding of Ag with the YBa₂Cu₃O₇ surface, as opposed to the effects of a pure Ag phase. The cutoff energy for 100- \AA Ag (on a Cu substrate, curve *e*) indicates a slight work function increase, compared to that of curve *b*.

Thus, we propose that the Ag affects mainly the surface

Cu–O bond configuration, which, in turn, dictates the relevant characteristics of the O diffusion process. The Ag-surface interaction may not necessarily imply weaker Cu–O bonds at the surface [actually, the heat of formation for CuO₂ is higher than that of CuO (Ref. 24)], but rather a surface rehybridization that decreases the electron spill over at the surface and therefore a decrease of the surface dipole layer. Thus, a negative O ion will feel the effect of a lower surface barrier. Such a change in the surface dipole is consistent with a higher convalency at the surface and with the trends reported in work-function values for oxidation of Cu.²⁵

In conclusion, we have observed a decrease in the barrier for oxygen out-diffusion in polycrystalline YBa₂Cu₃O_{7– δ} oxide samples without destroying its superconducting properties, by diffusing a coating of Ag into the samples. We have shown that Ag interacts with the surfaces (and possibly with the grain boundaries) to reduce the oxidation state of the surface Cu atoms, producing a surface with a lower work function. The lower work function most likely reflects a lower surface dipole and correlates with the lower value of the barrier for oxygen out-diffusion.

The authors would like to thank J. Berosh for sample preparation, P. Bailey for the SEM data, and V. L. Moruzzi and T. R. Dinger for helpful comments.

¹K. N. Tu, S. I. Park, and C. C. Tsuei, *Appl. Phys. Lett.* **51**, 2158 (1987).

²K. N. Tu, C. C. Tsuei, S. I. Park, and A. Levi, *Phys. Rev. B* **38**, 772 (1988).

³A. G. Schrott, S. L. Cohen, T. R. Dinger, F. J. Himpsel, J. A. Yarmoff, K. G. Frase, S. I. Park, and R. Purtell, in *Thin Film Processing and Characterization of High-Temperature Superconductors*, edited by J. M. E. Harper, R. J. Colton, and L. C. Feldman, AIP Conf. Proc. No. 165 (American Institute of Physics, New York, 1988), p. 349.

⁴P. D. Johnson, S. L. Qiu, L. Jiang, M. W. Ruckman, M. Strongin, S. L. Hulbert, R. F. Garret, B. Sinkovic, N. V. Smith, R. J. Cava, C. S. Jee, D. Nichols, E. Kaczanowicz, R. E. Salomon, and J. E. Crow, *Phys. Rev. B* **35**, 8811 (1987).

⁵A. Fujimori, E. Takayama-Muromachi, Y. Uchida, and B. Okai, *Phys. Rev. B* **35**, 8814 (1987).

⁶P. Steiner, V. Kisinger, I. Sander, B. Siegwart, S. Hüfner, and C. Politis, *Z. Phys. B* **67**, 19 (1987).

⁷R. L. Kurtz, in Ref. 3, p. 222.

⁸A. Bianconi, A. Congiu Castellano, M. De Santis, P. Delogu, A. Gargano, and R. Giorgi, *Solid State Commun.* **63**, 1135 (1987).

⁹D. E. Ramaker, in Ref. 3, p. 284.

¹⁰G. van der Laan, C. Westra, C. Haas, and G. A. Sawatzky, *Phys. Rev. B* **23**, 4369 (1981).

¹¹J. A. Yarmoff, D. R. Clarke, W. Drube, U. O. Karlsson, A. Taleb-Ibrahimi, and F. J. Himpsel, *Phys. Rev. B* **36**, 3967 (1987).

¹²A. Bianconi, A. Congiu Castellano, M. De Santis, P. Rudolph, P. Lagarde, A. M. Flank, and A. Marcelli, *Solid State Commun.* **63**, 1009 (1987).

¹³T. Gourieux, G. Krill, M. Maurer, M. F. Ravet, A. Menny, H. Tolentino, and A. Fontaine, *Phys. Rev. B* **37**, 7516 (1988).

¹⁴S. W. Tozer, A. Kleinsasser, T. Penney, D. Kaiser, and F. Holtzberg, *Phys. Rev. Lett.* **59**, 1768 (1987).

¹⁵R. Beyers, G. Lim, E. M. Engler, R. J. Savoy, T. M. Shaw, T. R. Dinger, W. J. Gallagher, and R. L. Sandstrom, *Appl. Phys. Lett.* **50**, 1918 (1987).

¹⁶W. M. Riggs and M. J. Palmer, in *Methods of Surface Analysis*, edited by A. W. Czanderna (Elsevier, New York, 1975), p. 157.

¹⁷T. J. Wagener, Y. Gao, I. M. Vitomirov, C. M. Aldao, J. J. Joyce, C. Capasso, and J. H. Weaver, *Phys. Rev. B* **38**, 232 (1988).

¹⁸M. Tang, N. G. Stoffel, Q. B. Chen, D. LaGraffe, P. A. Morris, W. A. Bonner, G. Margaritondo, and M. Onellion, *Phys. Rev. B* **38**, 897 (1988).

¹⁹T. E. Felter and W. H. Weinberg, *Surf. Sci.* **118**, 369 (1982).

²⁰C. Benndorf, M. Franck, and F. Thieme, *Surf. Sci.* **128**, 417 (1983).

²¹J. Eickmans, A. Goldmann, and A. Otto, *Surf. Sci.* **127**, 153 (1983).

²²C. Benndorf, H. Caus, B. Egert, H. Seidel, and F. Thieme, *J. Electron Spectrosc. Relat. Phenom.* **19**, 77 (1980).

²³K. Y. Yu, W. E. Spicer, I. Lindau, P. Pianetta, and S. F. Lin, *Surf. Sci.* **57**, 157 (1976).

²⁴I. Barin and O. Knacke, *Thermochemical Properties of Inorganic Substances* (Springer, Berlin, 1977).

²⁵S. Evans, E. L. Evans, D. E. Parry, M. J. Tricker, M. J. Walters, and J. M. Thomas, *Faraday Discuss.* **58**, 97 (1974).