# Electron spectroscopic evidence of metastable alloy formation of Ag and Au in Co

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High-resolution x-ray photoemission spectroscopy measurements of the conduction bands of dilute noble metal/Co metastable alloy films show a narrowing of the noble-metal *d* bands at concentrations below 6 at. % of noble metal consistent with coordination of the noble metal atoms with Co. Such alloying contrasts strongly with Ag and Au precipitation at higher concentrations, and with conventional metallurgical experience. It is consistent, however, with recent observations of modified interlayer exchange coupling in magnetic trilayer structures doped with noble-metal atoms [U. Ebels *et al.*, Phys. Rev. B **58**, 6367 (1998)]. [S0163-1829(99)05124-3]

# I. INTRODUCTION

Heterogeneous structures such as multilayers or granular films consisting of ferromagnetic and nonmagnetic metals show a large change of resistance in a varying external magnetic field.<sup>1</sup> For this giant magnetoresistance (GMR) effect to occur in granular films, the ferromagnetic grains have to be separated by the nonmagnetic matrix, so that there is no magnetic interaction between the grains and their magnetic moments are aligned randomly with respect to each other. In contrast, in multilayer GMR materials the ferromagnetic layers need to be coupled via an exchange interaction across the nonmagnetic metal spacer layer, so that the magnetizations in two neighboring ferromagnetic layers are aligned antiparallel when no external field is applied.<sup>1</sup>

Alloying and segregation of the two metals in these heterostructures are crucial in determining the GMR behavior. In granular films which generally consist of Co or Fe grains embedded in a noble-metal matrix, a high degree of segregation is desirable in order to obtain well-defined independent magnetic grains and a pure matrix. In multilayers, sharp interfaces are a prerequisite for antiparallel exchange coupling to occur.

The interlayer coupling in multilayers has been found to oscillate between parallel and antiparallel alignments of the magnetization in two neighboring ferromagnetic layers as the thickness of the nonmagnetic spacer layer increases with a period of the order of 10 Å. While the period of this oscillatory interlayer exchange coupling depends on the shape of the Fermi surface of the spacer layer metal, the amplitude and phase of the oscillations depend on the spin-dependent reflection coefficient at the interface and hence on the structure of the valence bands of both metals.<sup>2,3</sup>

Wigen and co-workers<sup>4,5</sup> deliberately modified the band structure of the top Co layers in Co/Cu/Co and Co/Ru/Co trilayer structures by adding between 2 and 8 at. % of noblemetal atoms which are expected to transfer extra electrons to the Co metal. This study successfully observed the phase of the oscillatory interlayer coupling to be shifted by up to 360°. Band-structure calculations for ordered fcc Co crystals show that the width of the valence band increases by 0.4 eV on replacing 6.25% of Co atoms by isolated Ag atoms.<sup>5</sup>

However, binary phase diagrams show that the solid solubility of Ag or Au in Co is less than 1 at. % at room temperature.<sup>6</sup> Hence it needs to be shown whether a metastable alloy with a modified band structure can be produced, or whether clusters of Ag or Au are always formed when Co is doped with these noble-metal atoms. Metastable alloys may be prepared by quenching the noble-metal/Co mixture by codeposition from two vapor sources onto a substrate or through melt spinning of a molten mixture onto a rotating cold wheel. However, for a high noble-metal concentration or an elevated substrate temperature, segregation will lead to the formation of granular materials. In the case of CoAg granular films with more than 20-at. % Ag, we have previously shown that there is no effect on the core levels of Co and Ag, and that the valence-band structure corresponds to a superposition of two independent bulklike metals.

If a metastable alloy of Co and Ag can be produced at low Ag concentrations, the Ag atoms will be in a very different environment from the Ag metal, and this should be reflected in changes of the Ag Auger parameter due to differences in the core-hole screening environment.<sup>8</sup> Variation of the local environmental potential due to a reduced number of Ag neighbors may lead to narrowing of the Ag 4*d* band which has previously been demonstrated for dilute Ag alloys with Mg (Ref. 9) and Al.<sup>10</sup> However, in contrast to these *sp* metals, Co has a 3*d* band at the Fermi energy, and hybridization with the noble-metal *d* electrons can occur. In addition, the resulting fluctuations in the local environment may cause a broadening of the core photoemission lines, as demonstrated experimentally<sup>11</sup> on CuPd and theoretically for a range of alloys.<sup>12-14</sup>

High-resolution x-ray photoemission spectroscopy (XPS) is suitable technique to study the structure of the valence band and at the same time have access to Auger and photoelectron transitions with higher binding energy to derive Auger parameters and study peak widths. In addition, the cross section for the Ag 4*d* electrons is approximately six times larger than for the Co 3*d* electrons,<sup>15</sup> which greatly enhances

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the sensitivity for studying low Ag concentrations. This study examines the properties of the CoAg and CoAu systems at low noble-metal concentrations using high-resolution electron spectroscopy to demonstrate possible alloying.

# **II. EXPERIMENT**

Noble-metal-doped Co films were fabricated by coevaporation onto commercial Si(111) wafer substrates. The concentration of noble metal atoms in the Co matrix was varied from 1 to 6 at. % by adjusting the metal flux ratios. The substrate temperature during deposition was kept below  $50 \,^{\circ}$ C to minimize diffusion-mediated segregation of the metals. The samples were rotated to ensure a homogeneous distribution of the noble metal atoms in the Co matrix. In addition, pure Co, Ag, and Au films were deposited as reference samples. All films were approximately 400 Å thick. *In situ* Auger measurements indicated segregation of Ag at the sample surface.

Photospectroscopy and Auger-electron spectroscopy measurements were carried out using the Scienta ESCA300 spectrometer at the Research Unit for Surfaces, Transforms, and Interfaces at Daresbury.<sup>16</sup> Electrons were excited with monochromated Al  $K_{\alpha}$  x-rays (hv = 1486.6 eV). The spot size at the sample surface was 6 mm long and 0.5 mm wide. The take-off angle  $\tau$  was 90°, i.e., normal to the surface, the hemispherical analyzer entrance slit 0.5 mm wide, the pass energy was 150 eV, and the base pressure was  $10^{-9}$  mbar. In measuring the binding energies of the sharper electron spectroscopic features a precision of better than 0.1 eV is possible, and resulting Auger parameter differences greater than 0.1 eV are likely to be significant at least for the core transitions of Ag. The broader Auger parameter values.

Prior to the spectroscopy measurements, the surface contaminants were removed through bombardment with 3-keV Ar ions under an angle of  $45^{\circ}$  at an Ar partial pressure of  $1 \times 10^{-6}$  mbar. After ion bombardment, survey spectra were recorded for all samples in order to confirm the cleanliness of the surface. The concentration of the probed surface region was determined from the area under the Co 2*p*, Ag 3*d*, and Au 4*f* photoelectron peaks after subtracting a linear background, and using sensitivity factors provided by the Scienta software.

For all Ag-doped Co samples, survey spectra show a much higher concentration of Ag than expected from the deposition fluxes confirming segregation of Ag at the sample surfaces. The fact that Ag was even found at the surface of a sample which contained a 30-Å-thick pure Co layer on top of the Ag-doped Co layer demonstrates the high mobility of Ag at room temperature. Further Ar-ion bombardment was carried out until the Ag concentration had reached a steady-state value. Spectra were then recorded at high resolution and over extended acquisition time for the valence band and the Auger electron and photoelectron transitons required to determine the Auger parameters. After performing these measurements over a period of typically 10 h, a contamination of the surface with 10 at. % of C and 3 at. % of O was observed.

### **III. RESULTS**

#### A. Valence band in Ag-doped Co

Valence-band (VB) XPS spectra for three-Ag-doped Co samples and the Co reference film are shown in Fig. 1. Two



FIG. 1. Valence-band spectra for three Ag-doped Co films and the Co reference film (detector entrance slit 0.5 mm, pass energy 150 eV). The dashed line represents a spectrum obtained by adding the pure Co and Ag valence-band spectra weighted by the respective concentrations for the  $Co_{5.5}Ag_{94.5}$  sample.

features of the VB structure change with increasing Ag concentration: (i) a shoulder, which originates from the Ag 4dband, emerges at approximately 6 eV and increases in height; and (ii) the intensity of the Co 3d band near the Fermi energy decreases.

In order to test whether these two observations reflect only the varying amounts of Co and Ag metal present in the films or whether they are an indication of alloy formation, the measured VB spectra for pure Co and Ag metal have been weighted by the atomic fractions of Co and Ag present in the probed surface region and superposed for each sample. The dashed line in Fig. 1 represents this superposition obtained from the pure Co and Ag reference VB spectra for the Co<sub>94.5</sub>Ag<sub>5.5</sub> sample. As is also the case for the other two Ag-doped Co samples, the superposition spectra reproduce neither the structure of the shoulder at approximately 6 eV nor the height of the Co 3d band near the Fermi energy, suggesting that Co and Ag do not behave like independent metals but form a metastable dilute alloy instead. This is in contrast to Ag-rich CoAg granular films studied previously, for which the structure of the measured VB could be well reproduced by superposing the weighted VB spectra of the pure elements.<sup>7</sup> From this it had been concluded that at high



FIG. 2. The valence-band spectrum for the Ag reference film and the differences between the CoAg alloy and the pure Co metal valence-band intensity from Fig. 1. The solid lines represent Gaussians fitted to determine the center and width of the peaks.

Ag concentration the two metals are well segregated and the observed VB spectrum arises from two independent metals.

In order to analyze the changes of the Ag electronic structure induced by doping Co with Ag atoms, the measured VB spectra for the Co reference film has been weighted by the Co concentrations present in the probed surface region and subtracted from the VB spectra for each Ag-doped Co sample. The difference spectra are shown in Fig. 2 together with the VB spectrum for a pure Ag film and Gaussians which have been fitted to the difference spectra in order to determine their width and center. The Ag contribution to the VB broadens from 1.6 to 2.8 eV, and its center shifts slightly from 6.0 to 5.7 eV with increasing Ag concentration. These values agree well with the Ag 4d-band-width of 2.0 eV measured for a MgAg alloy,<sup>9</sup> and 1.8 eV for a Al<sub>95</sub>Ag<sub>5</sub> alloy,<sup>10</sup> centered in both cases at 6.0 eV. The Ag VB structures for all Ag-doped Co films are clearly narrower than the 4d band of the pure Ag metal 3.4 eV wide (at a half height of the peak at approximately 4.5 eV) and centered at 5.5 eV; this compares well with previous XPS measurements for pure Ag [width 3.3 eV, center at 5.5 eV,<sup>17</sup> and width 3.6 eV, center at 5.6 eV (Ref. 9)]. A narrowing of the Ag band is expected for a reduced coordination with Ag neighbors, and has also been predicted theoretically for isolated Ag atoms embedded in a fcc Co crystal.5

With increasing Ag concentration not only do the position and width of the Ag contribution to the VB change toward pure Ag metal behavior, but the Ag metal doublet structure of the VB appears for the 5.5-at. % Ag sample, an effect which may arise from the presence of segregated Ag. In all three Ag-doped Co samples, the measured intensity of the Co 3d band near the Fermi energy is lower than expected from a superposition of the intensity for the pure metals.

#### B. Valence band in Au-doped Co

Figure 3 shows valence-band spectra for the Co sample doped with 5 at. % of Au and the pure Co reference film. As in the case of the Ag-doped Co samples, the structure of the



FIG. 3. Valence-band spectra for the  $Co_{95}Au_5$  alloy and the Co reference film (hemispherical analyzer entrance slit 1.9 mm, pass energy 300 eV). The dashed line represents a spectrum obtained by adding the pure Co and Au valence-band spectra weighted by the respective Co and Au concentrations.

Co<sub>95</sub>Au<sub>5</sub> VB cannot be reproduced by a superposition of the weighted spectra of the pure Co and Au films. The Au contribution to the Co<sub>95</sub>Au<sub>5</sub> VB spectrum obtained after subtracting the weighted pure Co VB spectrum is shown in Fig. 4 together with the pure Au reference film. The difference spectrum is 3.5 eV wide and centered at 6.2 eV, which is considerably narrower than the width of 5.8 eV of the 5*d* band centered at 5.0 eV for the pure Au reference film. This is to be compared with previous XPS measurements for pure Au [width 5.7 eV, center at 5.1 eV,<sup>18</sup> and width 5.4 eV, center at 4.3 eV (Ref. 19)]. As in the case of the Ag-doped Co films, it can be concluded that Au and Co do not behave like independent bulklike metals but that alloying occurs instead.



FIG. 4. The difference between the  $Co_{95}Au_5$  alloy and the pure Co metal valence band together with the valence-band spectrum for the Au reference film.

TABLE I. Auger parameters  $\alpha'$  for Ag-doped Co films.

Ag concentration (at. %)	$\frac{\alpha'(\text{Co}L_3 - L_3 M_{45} V)}{(\text{eV})}$	$\alpha'({\rm Ag}M_5 - M_5N_{45}N_{45}))$ (eV)
0	1551.8 (Ref. 7)	
0	1551.7	
0.9	1551.9	726.0
2.6	1551.9	726.2
5.5	1551.7	726.1
100		726.0
100		726.1 (Ref. 29)

# C. Auger parameters

Auger parameters for the Ag-doped Co samples and the pure metal reference films were obtained as in Ref. 7 and are listed in Table I together with the Auger and photoelectron transitions involved. The Auger parameters for Ag and Co vary by no more than 0.2 eV with respect to the values derived for the pure metals, which is close to the experimental uncertainty. Hence no significant affect on the core levels of Ag surrounded by Co atoms is observed. This was found previously for Ag-rich CoAg granular films, for which no evidence of metastable alloy formation was found.<sup>7</sup>

### **IV. DISCUSSION**

This paper has sought to clarify the electronic state of low concentrations of Ag and Au in thin Co films using electron spectroscopic studies of both core and valence levels. Highresolution XPS of the conduction bands of these materials conclusively demonstrates that the photoelectron spectra obtained for the noble-metal-doped Co films cannot be described in terms of an appropriately weighted superposition of the pure metal conduction bands. The observed narrowing of the Ag and Au d bands relative to those in the pure metal is a direct indicator of the change of noble-metal environment, and closely resembles what has been observed in other dilute alloys, e.g., Mg<sub>95</sub>Ag<sub>5</sub> (Ref. 9) and Al<sub>95</sub>Ag<sub>5</sub> and  $Cd_{97}Ag_3$ ,<sup>10</sup> where the overlap of the *d*-wave functions with the sp-wave functions of the adjacent metal atoms is much weaker than the d-d overlap in the pure metal, and less band broadening occurs. In the case of Ag- (Au-) doped Co, d-doverlap should dominate, but the density of states of Co 3d-like electrons is low in the energy region where that of Ag (Au) is high, and reduced overlap is thus still expected. This is confirmed in the calculations of Morkowski *et al.*<sup>5</sup> on hypothetically ordered fcc CoAg and CoAu alloys, with the noble metal atoms completely surrounded by Co. Using the linear muffin-tin-orbital method in the tight-binding atomic sphere approximation,<sup>20</sup> they demonstrated split-band behavior in these fictitious alloys with a narrow Ag band at higher binding energy than in the pure metal. Similar Ag d-band narrowing is found in FeAg alloys,<sup>21</sup> and Au d-band narrowing in PdAu,22 when the noble-metal concentration decreases.

The presence of Ag and Au will modify the effective Co density of states, an effect believed to be the reason for changes in the magnetic interlayer exchange coupling observed in multilayer systems.<sup>4,5</sup> The measurements presented

here show a small reduction in the apparent density of states at the Fermi level. However, the magnitude of this change is somewhat sensitive to the way in which the metal and alloy spectra are normalized relative to one another, and quantitative specification is difficult. Due to energy-loss processes on the high-binding-energy side of the band it is not possible to identify overall band broadening, which is predicted to be of the order of 0.5 eV.<sup>5</sup>

Since an alloy environment also changes the properties of the core electrons, both initial-state effects (environmental potential) and final-state shifts (extra atomic relaxation) in core photoemission and core-core-core Auger transitions are to be expected. It is possible to isolate changes in the screening environment through shifts in the Auger parameter  $\Delta \alpha$  $=\Delta E_B + \Delta E_{ccc}$ , given by the change in binding energy plus the change in Auger kinetic energy on alloying;<sup>8</sup>  $\Delta \alpha$  corresponds approximately to twice the change in extra atomic relaxation  $\Delta R_{ea}$  in the presence of a core hole. In metal alloys,  $\Delta \alpha$  values typically range between 0 and  $\pm 1$  eV (Refs. 23–25) and, if  $\Delta \alpha$  for both species can be determined, the  $\Delta \alpha$  values are usually of opposite sign. In the pioneering work of Thomas<sup>26</sup> and Thomas and Weightman,<sup>23</sup>  $\Delta \alpha$  was directly related to charge transfer in the alloy with the negatively charged atoms experiencing enhanced screening. Recent work by Cole and co-workers using an extended excited-atom model<sup>27,28</sup> reveals a more complex picture in which changes of population between d and sp character play an important role. In the case of metastable CoAg alloys, the  $3d_{5/2}$  photoemission and  $M_5N_{45}N_{45}$  Auger emission of Ag form a good pair of events to define an Auger parameter (Table I):  $\Delta \alpha \leq 0.2 \text{ eV}$  (the approximate experimental uncertainty), implying a screening environment closely similar to that of Ag metal. These results do not therefore directly support alloy formation. However, there are alloy systems, e.g., PdAg (Ref. 30) and AuAg,<sup>31</sup> where the Ag Auger parameter does not shift relative to the metal in contrast to PtAg, where  $\Delta \alpha \approx -0.8 \text{ eV.}^7$  For Co, no convenient core-core-core Auger transition is available—the  $L_{23}M_{23}M_{23}$  profile is very broad, while the  $L_3M_{23}V$  transition involves 3d electrons which are more bandlike than atomiclike. Furthermore at such low Ag concentrations, little change in the Co features is expected, a result consistent with observation.

Au has no suitable core-core Auger transition excited by Al  $K\alpha$  radiation, but the  $M_{45}N_{67}N_{67}$  transitions excited by Ti  $K\alpha$  may be readily combined with the  $4f_{7/2}$  or  $4f_{5/2}$  photoemission peaks to define a suitable Auger parameter. However, the Au  $M_5N_{67}N_{67}$  Auger intensity is extremely weak for low Au concentrations, and, as a result, the profile has to be measured at higher slit width (1.9 mm) and lower-energy resolution (300-eV pass energy) than for Ag. A significant positive 4f binding-energy increase (~0.7 eV) is observed in a Co<sub>95</sub>Au<sub>5</sub> alloy film relative to Au metal, but the Auger parameter changes are smaller, and again evidence of alloying for the core-electron spectra is inconclusive.

Recent work by Cole and co-workers<sup>11–13</sup> and Faulkner, Wang, and Stocks<sup>14</sup> demonstrated how core photoemission peaks broaden in disordered alloys due to variation in the number of like and unlike neighbors, causing variation in the local environment potential. It is therefore of interest to investigate how the breadth of the 3*d* photoemission lines of Ag in Co vary with Ag concentration. Broadening can



FIG. 5. Comparison of the Ag  $3d_{5/2}$  photoelectron emission peaks of pure Ag metal and 0.9 at. % of Ag in Co normalized to the same area.

clearly be seen from comparison of the Ag  $3d_{5/2}$  peaks in Fig. 5 for 0.9 at. % of Ag in Co, with the pure Ag metal normalized to the same area. The  $3d_{5/2}$  photoemission peaks are fitted with Voigt profiles of full width at half maximum  $\Gamma$ and an asymmetry index<sup>16</sup> which is found to vary little with composition. Figure 6 combines data for the  $3d_{5/2}$  breadth  $\Gamma$ from the previous study on CoAg granular films<sup>7</sup> with this work. The same experimental conditions (slit width 0.5 mn, pass energy 150 eV) were used in both experimental runs, and so the data should be directly comparable. For the pure Ag reference film  $\Gamma(3d_{5/2}) = 0.55$  eV, as observed previously under identical conditions.<sup>16</sup> For high Ag concentrations, for which segregation occurs, the breadth is similar to that of the pure metal, but at the lower concentrations  $\Gamma(3d_{5/2})$  significantly increases up to approximately 0.9 eV at 0.9 at. % of Ag in Co. This suggests that a range of Ag environments evolves with Ag atoms bonded to Ag neighbors becoming less important as the Ag concentration decreases. The enhancement in broadening is comparable to



FIG. 6. Variation of the full width at half maximum (FWHM) of the Ag  $3d_{5/2}$  photoelectron emission peak in CoAg with Ag concentration.

that found in other alloy systems.<sup>11–14</sup> The picture, then, is one of a gradual diminishing in Ag segregation giving way to diverse local Ag coordination with associated fluctuations in the local potential at low Ag concentrations.

In summary, the conduction-band profiles of dilute Ag or Au in Co determined by high-resolution XPS provide strong evidence for the noble metals forming a disordered alloy with Co under conditions where segregation is to be expected at thermodynamic equilibrium. In addition, core photoemission peak broadening gives strong evidence for alloying at a low noble-metal concentration. However, the Ag Auger parameter changes little relative to Ag metal. Overall the results confirm that small additions of Ag or Au to thin Co films will change the electronic structure of the film in a manner that may lead to the observed modified interlayer exchange coupling in magnetic multilayers.<sup>4,5</sup>

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- <sup>1</sup>*Ultrathin Magnetic Structures*, edited by B. Heinrich and J. A. C. Bland (Springer, Berlin, 1994), Vol. 2, Chap. 2.
- <sup>2</sup>P. Bruno, J. Magn. Magn. Mater. **121**, 248 (1993).
- <sup>3</sup>M. D. Stiles, Phys. Rev. B **48**, 7238 (1993).
- <sup>4</sup>P. E. Wigen, L. Zhou, R. Stamps, K. Ounadjela, M. Hehn, and J. F. Gregg, J. Magn. Magn. Mater. **165**, 465 (1997).
- <sup>5</sup>U. Ebels, R. L. Stamps, L. Zhou, P. E. Wigen, K. Ounadjela, J. Gregg, J. A. Morkowski, and A. Szajek, Phys. Rev. B 58, 6367 (1998).
- <sup>6</sup>Constitution of Binary Alloys, edited by M. Hansen (McGraw-Hill, New York, 1958).
- <sup>7</sup>M. Gester, J. A. D. Matthew, S. M. Thompson, K. Ounadjela, and G. Beamson, Surf. Interface Anal. **26**, 32 (1998).
- <sup>8</sup>C. D. Wagner and A. Joshi, J. Electron Spectrosc. Relat. Phenom. 47, 283 (1988).
- <sup>9</sup>P. Weightman, P. T. Andrews, and A. C. Parry-Jones, J. Phys. C 12, 3635 (1979).

- <sup>10</sup>R. J. Cole, J. A. Evans, L. Duò, A. D. Laine, P. S. Fowles, P. Weightman, G. Mondio, and D. Norman, Phys. Rev. B 46, 3747 (1992).
- <sup>11</sup>R. J. Cole and P. Weightman, J. Phys.: Condens. Matter **10**, 5679 (1998).
- <sup>12</sup>R. J. Cole, N. J. Brooks, and P. Weightman, Phys. Rev. Lett. 78, 3777 (1997).
- <sup>13</sup>R. J. Cole and P. Weightman, J. Phys.: Condens. Matter 9, 5609 (1997).
- <sup>14</sup>J.S. Faulkner, Y. Wang, and G. M. Stocks, Phys. Rev. Lett. 81, 1905 (1998).
- <sup>15</sup>J. H. Schofield, J. Electron Spectrosc. Relat. Phenom. 8, 129 (1976).
- <sup>16</sup>G. Beamson and D. Briggs, *High Resolution XPS of Organic Polymers* (Wiley, Chichester, 1992).
- <sup>17</sup>S. Hüfner, G. K. Wertheim, N. V. Smith, and M. M. Traum, Solid State Commun. **11**, 323 (1972).

- <sup>18</sup>S. B. M. Hagström, *Electron Spectroscopy*, edited by D. A. Shirley (North-Holland, Amsterdam, 1972), p. 515.
- <sup>19</sup>Y. Baer, P-F. Heden, J. Hedman, M. Klasson, C. Nordling, and K. Siegbahn, Phys. Scr. 1, 55 (1970).
- <sup>20</sup>O. K. Andersen, O. Jepsen, and M. Sob, in *Electronic Structure and its Applications*, edited by M. S. Yussouff (Springer, Berlin, 1987); G. Krier, O. Jepsen, A. Burkhardt, and O. K. Andersen, LMTO-ASA Program (source code, version 4.7).
- <sup>21</sup> M. Ushida, K. Tanaka, K. Sumiyama, and Y. Nakamura, J. Phys. Soc. Jpn. **58**, 1725 (1989).
- <sup>22</sup>R. I. R. Blyth, A.B. Andrews, A. J. Arko, J. J. Joyce, P. C. Canfield, and B. I. Bennet, Phys. Rev. B 49, 16 149 (1994).
- <sup>23</sup>T. D. Thomas and P. Weightman, Phys. Rev. B 33, 5406 (1986).
- <sup>24</sup>C. G. G. Walker, S. A. Morton, G. Beamson, J. A. D. Matthew, and F. N. Yousif, J. Electron Spectrosc. Relat. Phenom. **70**, 73

(1994).

- <sup>25</sup>J. A. D. Matthew, S. A. Morton, C. G. H. Walker, and G. Beamson, J. Phys. D 28, 1702 (1995).
- <sup>26</sup>T. D. Thomas, J. Electron Spectrosc. Relat. Phenom. **20**, 117 (1980).
- <sup>27</sup>R. J. Cole, D. A. C. Gregory, and P. Weightman, Phys. Rev. B 49, 5657 (1994).
- <sup>28</sup>R. J. Cole, J. A. D. Matthew, and P. Weightman, J. Electron Spectrosc. Relat. Phenom. **72**, 255 (1995).
- <sup>29</sup>D. Briggs and M. P. Seah, *Practical Surface Analysis* (Wiley, Chichester, 1990), Vol. 1.
- <sup>30</sup>T. M. Grehk, W. Drube, G. Materlik, J. E. Hensen, and T. K. Shen, J. Electron Spectrosc. Relat. Phenom. 88–91, 241 (1998).
- <sup>31</sup>G. G. Kleiman, R. Landers, and S. G. C. Castro, J. Electron Spectrosc. Relat. Phenom. **72**, 199 (1995).