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T Kaurila, L Säisä and J Väyrynen

Laboratory of Materials Science, Department of Applied Physics, University of Turku, Itäinen Pitkäkatu 1, FIN-20520 Turku, Finland

Abstract. The resonant photoemission of iron films on copper has been examined near the 3p→3d excitation threshold using synchrotron radiation from the MAX storage ring. Resonant profiles are presented in the photon energy range 44–150 eV. Special attention has been paid to the position of the destructive minimum before the enhancing resonance. The results reveal that the interaction between the valence bands of iron and copper is weak in terms of autoionization. Moreover, our data do not support the conclusion about the subthreshold Auger emission reported earlier for iron.

1. Introduction

Transition metals are an interesting object of research in many respects, particularly in terms of photoemission, which provides information about the electronic structure and properties of materials. Firstly transition metals are commonly used in catalyzed synthesis in industry. For example the Haber process for the preparation of ammonia involves an iron–iron oxide catalyst. Secondly at atomic level they possess an open d shell, whereas in the metallic phase the band-like behaviour is notably more dominant than the atomic-like behaviour. Thirdly each transition metal generally has several accessible oxidation states. Furthermore their magnetic character varies from paramagnetic to ferromagnetic and their oxides can undergo a metal–insulator phase transition. It has also been suggested that ultrathin layer of certain transition metals can exhibit surface magnetic moments [1–4].

Resonant photoemission of the first transition metal series and satellites related closely to the phenomenon have been quite intensively studied in past decades [5–9 and references therein]. In the case of iron, treatment and emphasis have been concentrated primarily on the existence of the 6 eV satellite but, for instance, the shape of the resonant profile of the valence band is poorly known in the wider photon energy range [6, 10–14]. Besides, some investigations have been carried out by the EELS or the Auger technique making accurate comparison of the results laborious [15–17]. Finally there exists a problem, oxygen contamination, seen as the ~ 6 eV peak in the binding energy scale. If one handles spectra incorrectly the oxygen peak seems to resonate as a normal satellite does.

Resonant photoemission, also called autoionization, near the 3p threshold can be described in atomic notation as the interference between the normal photoemission $3p^6 3d^6 4s^2 + h\nu \rightarrow 3p^6 3d^5 4s^2 + e^-$ and the decay of the core excitation as $3p^5 3d^7 4s^2 \rightarrow 3p^6 3d^5 4s^2 + e^-$, where the 3p electron has been excited firstly into an unoccupied state above the Fermi level. As a result of the latter transition a valence electron is emitted at the same kinetic energy as an ejected photoelectron. Interaction of these two de-excitation channels causes the intensity of the 3d band to decrease at photon energies near the 3p threshold energy. On the other hand above the threshold the intensity of the 3d peak

enhances significantly. Fano was the first to develop a theory to describe the autoionization phenomenon [18]. Another visible event that can be detected in a valence band spectrum is a super-Coster–Kronig (SCK) peak, which appears with photon energies higher than the 3p excitation energy. This $M_{2,3}M_{4,5}M_{4,5}$ Auger transition arises from the de-excitation of the 3p hole state i.e. a valence electron fills the 3p hole and simultaneously another valence electron known as an Auger electron is ejected at a constant kinetic energy. Consequently the Auger transition and the autoionization are the competing decay processes of the 3p excitation.

In this paper we have considered autoionization of an iron film as a function of thickness on a copper substrate around the 3p threshold of iron (52.8 eV). We will pay special attention to the resonant behaviour of the valence band by examining resonant profiles, i.e. height of peaks versus photon energy. In the studies resonant photoemission of clean copper has been measured in order to take into account the influence of the substrate. After this we will deal with the subthreshold Auger emission of iron and with extracted energy values of the $M_{2,3}M_{4,5}M_{4,5}$ transitions. The last part will be devoted to the intensity correction of monochromatized flux of synchrotron light, which is an essential task in analysing measurements such as ours.

2. Experimental details

The research was carried out at the beamline 41 (BL41) of the MAX synchrotron radiation facility in Lund, Sweden. The beamline has been equipped with a toroidal grating monochromator (TGM) and an angle resolved hemispherical electron energy analyser. For the experiments we connected our own preparation chamber to the main chamber of BL41. The chamber included an effusion cell, wire evaporators, a sputter gun and an electron bombardment heater for processing of samples and a LEED camera. The measurements were performed in the photon energy range 44–150 eV while the total resolution determined from widths of the Fermi level varied between 0.35 eV and 0.5 eV. The energy calibration of the spectra was also done by means of derivated Fermi edges.

We prepared iron films by evaporating iron from a high-purity wire onto a copper substrate. The mechanically polished substrate was cleaned by several cycles of argon ion sputtering (4 keV→2 keV→1 keV→0.5 keV) and annealing up to 500 °C. To avoid surface contamination the iron wire was outgassed carefully before depositions and pressure was kept lower than 1×10^{-9} Torr during evaporations. The cleanness of the surface was checked by employing the 2p peak of oxygen located about 6 eV below the Fermi edge: if the peak does not appear in the spectra, the surface can be regarded as free from contaminants. This assumption is based on the following facts. Firstly the photoelectron measurements of the valence band are very surface sensitive in the photon energy range used. Equally the cross section of the O 2p level is high in this photon energy region [19]. Lastly, since the transition metals are exceptionally reactive, one might expect that oxygen and its compounds are the major impurities on the surface. In spite of our carefulness we were not able to totally avoid surface contamination. The peak induced by oxygen can be seen as an observable feature in spectra measured from a thick iron layer corresponding to bulk iron.

The intensity ratio of the 3d peaks of copper and iron and the exposure time were employed to control the thickness of the iron layer. Determined values are in good agreement with the thickness obtained by Polzonetti et al in [20] for corresponding spectra. Emitted electrons were detected at normal emission and the angle between the surface normal and the incident beam was 54.7° corresponding to the magic angle. Hence angular effects have been minimized in the measurements.
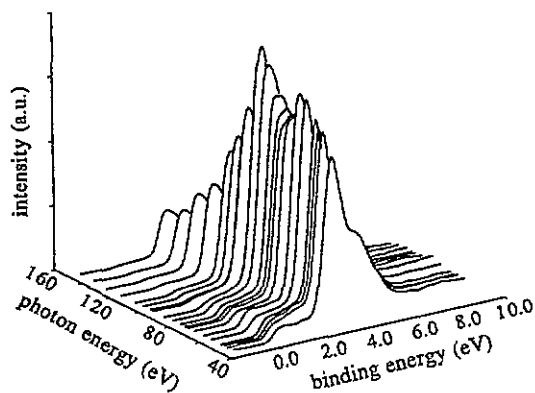
Figure 1. Photoelectron spectra from the valence band of copper with different photon energies.

3. Results and discussion

Figure 1 shows a series of valence band spectra taken from a clean copper substrate with exciting energies 46–150 eV. Intensities of the photoelectron spectra in this work have been corrected by an optical absorption spectrum of gold [21]. We do not consider the correction of the intensity more exactly now, because we will return to it later. The spectra of copper do not exhibit a strong resonance. This can be predicted from the band structure calculation [22], since copper has only a few unoccupied states into which a 3p electron can be excited. At photon energies higher than 90 eV the intensity of the valence band falls quite rapidly owing to the decrease of the cross section of the valence band [19] and the absence of appropriate excited states for autoionization.
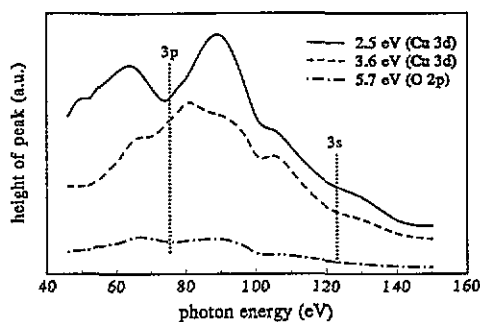

Figure 2. Resonant profiles from the 3d band of copper and from the 2p peak of oxygen. The ionization thresholds of copper 3s and 3p are also indicated.
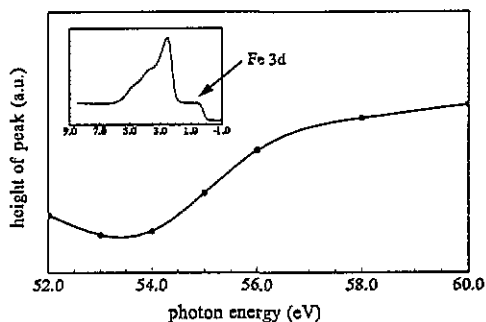
Figure 3. The resonant profile of the 2–3 Å iron film around the destructive interference. The curve has been taken with a binding energy of 1 eV. The inset presents the valence band spectrum excited with 60 eV photons.

Let us now study more closely resonant profiles of Cu constructed by plotting heights of peaks as a function of photon energy. The 3d band of copper splits partly to two components: the lower band consists mainly of the d and s type atomic orbitals whereas the upper one has more p character than s character [22]. As a result of this splitting we have produced two profiles at constant binding energies of 2.5 eV and 3.6 eV (figure 2). In addition the profile of the 2p peak of oxygen has been shown in order to see the behaviour of the background.

Now the characteristic Fano line shape is clearly seen: the destructive interference takes place slightly below the 3p→3d excitation and the successive constructive interference approaches a maximum at a photon energy of approximately 89 eV for the 2.5 eV band. The autoionization effects are not so significant in the lower profile of copper as in the upper one, which matches well with the absorption spectrum measured by Sonntag *et al* [23]. However, excluding the position of the maximum occurring already at photon energy of 80 eV the profiles of copper look quite similar.

An additional weak shoulder appearing near the 130 eV photon energy can be probably related to the autoionization resulting from the excitation from 3s to unoccupied states above the Fermi level. The weakness of the structure can be explained by the fact that the valence band of copper is composed mostly from the d type atomic orbitals and only in a tiny degree from the p and s orbitals according to the band structure calculations. When the dipole selection rules only allow a change of ± 1 in the angular momentum it is easy to understand that the excitation cross section remains low. Another variation of the intensity of the 3d band above the Fano interference occurs in the photon energy range 105–110 eV. To explain this we refer to atomic calculations where the cross section of Cu 3p shows a Cooper minimum around 110 eV [19], so we suggest that the small fluctuation above 100 eV in the profiles originates from a similar factor as the Cooper minimum. Radial nodes of the initial state 3p wavefunction cause a dip in the transition probability at a certain photon energy. At photon energies of 105–110 eV the intensity of the valence band still contains contributions from both the 3d photoemission and the 3p→3d autoionization and therefore this effect becomes possible to observe.

Now we can proceed to the autoionization of the iron film with a thickness of 2–3 Å (figure 3). The inset of the figure shows the valence region excited with 60 eV photons. The visible enhancement of the valence band just below the Fermi level is related primarily to the emergence of the 3d band of iron. Otherwise the spectrum resembles the corresponding spectrum of copper in figure 1. On account of the thinness of the layer the resonance of iron remains weak and the peaks of copper dominate the region of the valence band. For this reason figure 3 depicts only the destructive interference of the resonance. The minimum for the 3d band of iron occurs at a photon energy of 53.5 eV, which is slightly higher than the 3p binding energy (see table 1). The evaluated position of the minimum agrees reasonably precisely with those presented in [6], [10] and [13] for single crystals of iron.

Table 1. Extracted values for the 3p binding energy and the Auger MMM kinetic energy of iron and copper (in electron volts) agree well with the values given in [6] and [15].

	$E(3p_{1/2})$	$E(3p_{3/2})$	$E_{kin}(M_{2,3}M_{4,5}M_{4,5})$
Fe	53.5 ± 0.1	52.5 ± 0.1	48.6 ± 0.3
Cu	77.16 ± 0.1	74.89 ± 0.1	$63.7, 60.8 \pm 0.2$

Figure 4 represents valence band spectra where 8–9 Å of iron has been deposited on copper. Now the valence band of iron plays the major role and one can see that the resonance of iron is much more effective than the resonance of copper in the figure 1. Moreover, the SCK peak, indicated by A, appears above the 3p→3d excitation and moves toward higher binding energy with increasing photon energy.

To see resonant structures more clearly we have performed profiling at three constant binding energies for the spectra illustrated in figure 4. The results are shown in figure 5. The first profile has been taken at a binding energy of 0.85 eV and containing predominantly
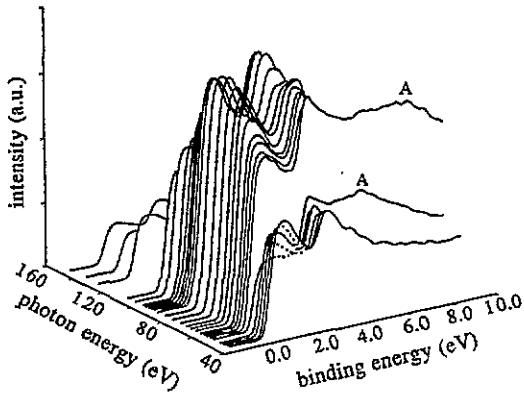
Figure 4. Energy distribution curves from the valence band where the thickness of the iron layer is 8–9 Å. The SCK peak of iron has been labelled A.
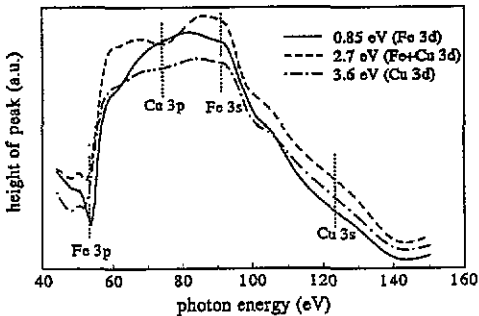

Figure 5. Resonant profiles from the valence band spectra shown in figure 4. The vertical lines display the positions of the 3p and 3s thresholds.
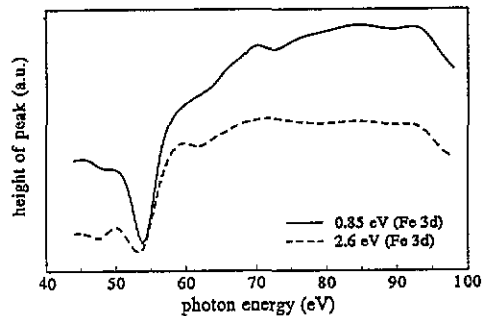
Figure 6. Resonant profiles of the bulk iron with two different energies.

the contribution of the 3d band of iron; the second one has been taken at an energy of 2.7 eV, where the valence bands of iron and copper overlap, and the last contour has been generated from the lower part of the 3d band of copper at a binding energy of 3.6 eV. The major features of copper are still observed through the iron overlayer except that the level of the intensity increases strongly above the photon energy of 53.5 eV as a result of the autoionization of iron. On the other hand the shape of the 0.85 eV profile, *originating mainly from iron, differs significantly from the profiles of copper. The most striking difference emerges as a great fluctuation between the destructive and constructive interference. Moreover the resonance of iron spreads over a region of 65 eV whereas for copper the width of the resonant photoemission is only about 40 eV. The reason for both phenomena can be found presumably in the electronic configurations of iron and copper, which are $3d^6 4s^2$ and $3d^{10} 4s$ in atomic notation, respectively. Thus iron has more empty states available for the core excitation in terms of strong autoionization. In the same way these unoccupied states expand the width of the resonant region, offering the possibility of shake-up processes such as $3p^6 3d^6 4s^2 + h\nu \rightarrow 3p^5 3d^{7-1} 4s^2 nl$, where nl denotes the excited shake-up electron. The interpretation of the enhancement near 130 eV attributed to the 3s→3d autoionization of copper is confirmed too, because the profile dominated by the 3d band of iron exhibits only a very weak increase.

Resonant profiles of a thick iron layer, thicker than 40 Å, are displayed in figure 6 at

photon energies between 44 and 98 eV. Since the inelastic mean free path of photoelectrons varies from 3 Å to 4 Å at the energies used [24], the experiment is very surface sensitive and the signal from the 3d band of copper vanishes completely. Hence the 40 Å thick iron film can be regarded as the bulk substance.

Let us begin by taking an overview of the profiles corresponding to the bulk iron. The position of the minimum occurring at a photon energy of 53.5 eV does not shift with the thickness of the iron film. Furthermore, the general shape of the upper profile brings up the same details as the curve obtained for an iron layer of 8–9 Å. Consequently it seems that there exists only a weak interaction between the valence bands of iron and copper. The interaction is expected to be very weak since the metals do not form alloys [25] and therefore only the contact layer between copper and iron can modify their electronic structure. In principle we might detect changes due to the layer of adhesion with the film of a few monolayers, because the measured signal originates only from a few outermost atom layers. Comparing our profile of the 3d band to the cross section given by Chandesris *et al* in [6] one can discover many contrasts. The most apparent difference is the trend of the cross section; it increases in this work while it has a decreasing tendency in [6], so it seems that Chandesris *et al* have normalized the spectra by a different method from ours. In the same way as with the profiles of the clean copper, we propose that the minimum above 70 eV could be assigned to the Cooper minimum of the 3p peak of iron [19].
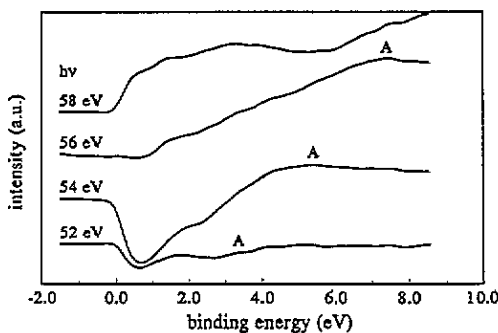

Figure 7. The appearance of the SCK peak near the 3p excitation. The difference EDCs have been obtained by subtracting the reference EDC ($h\nu = 50$ eV) from 52, 54, 56 and 58 eV EDCs. The original spectra have been scaled according to the incident photon flux. A indicates the position of the Auger peak.

To investigate the appearance of the SCK transition in iron in the vicinity of the 3p threshold (52.8 eV) we have subtracted the energy distribution curve (EDC) excited by 50 eV from EDCs of 52, 54, 56 and 58 eV. Prior to the subtraction the spectra have been scaled according to the intensity of the incident light. The result can be seen in figure 7. Walker *et al* [13] reported an Auger distribution even below the 3p excitation threshold but we did not find any evidence from the Auger signal related to SCK at a photon energy of 52 eV. Our first observation of SCK appears at a photon energy of 54 eV with a kinetic energy of 48.6 eV with respect to E_F, which is in excellent agreement with the value measured by Ramsey and Russell [16]. Owing to the rough step (2 eV) of the exciting energy we cannot deduce anything about the existence of an SCK peak near the 3p threshold. One solution for the dissimilar conclusions might be found from the methods of normalization of the reference EDC: before subtraction Walker *et al* scaled the spectra to the same 3d

peak heights, whereas we have normalized according to the incident photon flux. Since valence bands have different symmetries, consisting of the e_g and t_{2g} components, they can resonate unsimultaneously and by different powers. An example of this can be seen in figure 6. Another reason for the disagreement could be the different samples: single crystal and polycrystal. Thirdly the amount of surface contamination can affect the Auger emission significantly. Despite the disagreement concerning the subthreshold Auger emission in iron, it is obvious that the probability of SCK increases at the cost of the valence band emission to satisfy the sum rule for the intensities as Walker *et al* have mentioned.

In addition to the resonant photoemission we have measured the binding energy of the 3p level and the kinetic energy of the SCK peak in both the metals with photon energies considerably above the 3p excitation energy. These results are summarized in table 1. The spin–orbit splitting of the peaks is resolved clearly in the EDCs except in the case of the SCK of iron, which might be due to the splitting of 3p being only 1.0 eV. Furthermore the width of the valence band, which is broader for iron than for copper, can stretch the Auger distribution. The kinetic energy of the MVV Auger can also be estimated with the aid of the simple relation $E_{\text{Auger}} = E_{3p} - 2E_{3d} - U_{\text{eff}}$ [26]. Here U_{eff} is the Coulomb correlation between two 3d holes and the other energies on the right hand side of the equation correspond to the binding energy of the 3p core level and the 3d band. For the calculated SCK energies one obtains, using the values presented in table 2, 48.2 eV for iron and 62.6 eV and 60.3 eV for copper, respectively. Accordingly the results suggest that the Coulomb repulsions between the d holes applied in the calculation are quite valid in both cases.

Table 2. Calculated MMM Auger energies and binding and correlation energies required in calculations (in electron volts) are presented for iron and copper. U_{eff} has been obtained from [27] and U_{eff} in parenthesis from [28]. $E(3d)$ has been estimated from the measured data.

	$E(3p)$	$E(3d)$	U_{eff}	$E_{\text{kin}}(M_{2,3}M_{4,5}M_{4,5})$
Fe	52.8	1.0	2.6(1)	48.2
Cu	77.2, 74.9	3.0	8.6(8)	62.6, 60.3

To conclude this section we return again to the normalization of the EDCs with respect to the incident photon flux. The intensity of monochromatized light is often determined by measuring photocurrent of the gold net. This is also done at BL41 in Max-laboratory but the analysing system ignores the wavelength dependence of the photocurrent. For this reason, if one wants to present EDCs taken with different photon energies on an absolute or comparable scale, EDCs have to be rescaled with the quantum efficiency of gold corresponding to the optical absorption spectrum.

At BL41 in Max-laboratory the flux of the monochromatized light is measured using a pulse counting technique via an electrometer and a voltage–frequency converter. The data acquisition time for each channel in the spectrum is the time required to reach a preset number of counts from the gold net. However the counts from the gold net do not include information about the quantum yield of gold. To correct errors due to the wavelength dependence of the photocurrent we have multiplied EDC counts by the absorption coefficient of gold. The optical absorption spectrum we have used in this work was measured by Hagemann *et al* in the DESY synchrotron light source in Hamburg [21].

Even if the correction mentioned above is executed one cannot be completely sure that all contributions modifying intensity have been eliminated. Typical sources of errors are spot size, second-order light or misalignment of sample and analyser. Moreover the execution

order of the background subtraction and the normalization plays a meaningful role; only in the situation of the uniform background is there no difference whichever procedure is taken first.

4. Conclusions

The resonant profiles have been presented for clean copper and iron films of several different thicknesses on copper. Features of the profiles can be explained by the electronic configuration of these metals. Moreover the experiments show that no detectable interaction between the valence bands of the metals in terms of autoionization occurs. Our energy distribution curve for a thick iron layer also does not exhibit the subthreshold Auger emission below the 3p excitation energy reported earlier by others.

Acknowledgments

References

[1]   Ohnishi S, Freeman A J and Weinert M 1983 *Phys. Rev.* B **28** 6741
[2]   Wimmer E, Freeman A J and Krakauer H 1984 *Phys. Rev.* B **30** 3113
[3]   Binns C, Derbyshire H S, Bayliss S C and Norris C 1992 *Phys. Rev.* B **45** 460
[4]   Fu C L and Freeman A J 1986 *Phys. Rev.* B **33** 1755
[5]   Davis L C 1986 *J. Appl. Phys.* **59** R25
[6]   Chandesris D, Lecante J and Petroff Y 1983 *Phys. Rev.* B **27** 2630
[7]   Guillot C, Ballu Y, Paigné J, Lecante J, Jain K P, Thiry P, Pinchaux R, Pétroff Y and Falicov L M 1977 *Phys. Rev. Lett.* **39** 1632
[8]   Björneholm O, Andersen J N, Wigren C, Nilsson A, Nyholm R and Mårtensson N 1990 *Phys. Rev.* B **41** 10408
[9]   Davis L C and Feldkamp L A 1981 *Phys. Rev.* B **23** 6239
[10] Kato H, Ishii T, Masuda S, Harada Y, Miyano T, Komeda T, Onchi M and Sakisaka Y 1985 *Phys. Rev.* B **32** 1992
[11] Chandesris D, Lecante J and Petroff Y 1986 *Phys. Rev.* B **34** 8971
[12] Kato H, Ishii T, Masuda S, Harada Y, Miyano T, Komeda T, Onchi M and Sakisaka Y 1986 *Phys. Rev.* B **34** 8973
[13] Walker K-H, Kisker E, Carbone C and Clauberg R 1987 *Phys. Rev.* B **35** 1616
[14] Raaen S and Murgai V 1987 *Phys. Rev.* B **36** 887
[15] Ramsey M G and Russell G J 1984 *Phys. Rev.* B **30** 6960
[16] Ramsey M G and Russell G J 1985 *Phys. Rev.* B **32** 3654
[17] Zajac G, Bader S D, Arko A J and Zak J 1984 *Phys. Rev.* B **29** 5491
[18] Fano U 1961 *Phys. Rev.* **124** 1866
[19] Yeh J J and Lindau I 1985 *At. Data Nucl. Data Tables* **32** 1
[20] Polzonetti G, Di Castro V, Contini G and Ciampi S 1992 *J. Electron Spectrosc. Relat. Phenom.* **58** 23
[21] Hagemann H-J, Gudat W and Kunz C 1975 *J. Opt. Soc. Am.* **65** 742
[22] Papaconstantopoulos D A 1986 *The Handbook of the Band Structure of Elemental Solids* (New York: Plenum)
[23] Sonntag B, Haensel R and Kunz C 1969 *Solid State Commun.* **7** 597
[24] Seah M P and Dench W A 1979 *Surf. Interface Anal.* **1** 2
[25] Moffat W G 1978 *The Handbook of Binary Phase Diagrams* (New York: General Electric)
[26] Ramsey M G and Russell G J 1985 *Appl. Surf. Sci.* **22/23** 206
[27] Yin Lo I, Tsang Tung and Adler Isidore 1977 *Phys. Rev.* B **15** 2974
[28] Antonides E, Janse E C and Sawatzky G A 1977 *Phys. Rev.* B **15** 1669