PHYSICAL REVIEW B VOLUME 47, NUMBER 24 15 JUNE 1993-II

Low-energy electron-energy-loss spectroscopy of Eu, Gd, and Tb: 5s and 5p excitations

J. Kołaczkiewicz
Institute of Experimental Physics, University of Wrocław, ulica Cybulskiego 36, 50-205 Wrocław, Poland

E. Bauer
Physikalisches Institut der Technischen Universitat Clausthal, Leibnitzstrasse 4, D-3392 Clausthal-Zellerfeld, Germany
(Received 28 December 1992)

The electronic structure of Eu, Gd, and Tb layers deposited on tungsten (110) and (211) surfaces was investigated by electron-energy-loss spectroscopy in the energy range from 20 to 50 eV. Losses previously assigned to plasmon excitation are shown to be due to multiple excitations.

I. INTRODUCTION

The surfaces of rare-earth metals have received considerable attention because their electronic structure differs particularly strongly from that of the bulk.[1] Photoemission and inverse-photoemission spectroscopy (IPES) as well as low-energy electron energy-loss spectroscopy (EELS) have been the major tools which have given considerable insight into the complex electronic structure and photon- or electron-induced electronic transitions. The interpretation of the spectra is not always unambiguous. For example, the energy-loss spectra due to core-level excitations usually contain losses with larger loss energy than the ionization energy, which in the case of the $4d$ spectra have been attributed to autoionization,[2–6] but in the case of the $5p$ spectra to multiple plasmon excitation.[7]

In the present paper we examine whether or not the $5p$ spectra really contain a plasmon loss contribution or whether this can also be explained by a correlated one—electron processes. We do this (i) by studying the dependence of the spectra upon the primary electron energy, which allows us to vary the sampling depth and the excitation conditions; (ii) by studying the coverage dependence of the spectra of rare-earth adsorption layers on W (110) and (112), which allows us a comparison between the quasiatomic state at coverages below the work-function minimum $\phi_{\min}$ and the two-dimensional condensed state at coverages above $\phi_{\min}$. Plasmons can exist above $\phi_{\min}$ but not below.

Rare-earth metals strongly lower the work function of pure tungsten, similar to alkali and alkaline earth metals. This has frequently been attributed to a valence-electron transfer from the adsorbate to the substrate.[8–12] The present study is also aimed at examining this question. Previous Auger electron spectroscopy studies indicate that recombination transitions of the $4d$ level involving valence electrons occur only at coverages above $\phi_{\min}$. However, this does not solve the question of whether the valence electrons are transferred to the substrate below $\phi_{\min}$, or can recombination transitions not be realized in the atomiclike electron configuration below $\phi_{\min}$ in which the $6p$ electrons necessary for an optically allowed recombination process to the $4d$ level are missing. Electron transfer to the substrate should be evident in energy-loss spectra involving transitions to and from valence states which are occupied in the neutral state of the atom but lose some of their occupation in the ionized state. For the $6s$ and $5d$ valence electrons, transitions to and from p levels are allowed. The $5p$ level has the lower binding energy and is, therefore, particularly suitable for an EELS experiment. Our studies focus on the rare-earth metals Eu, Gd, and Tb. Gd and Tb are trivalent in the metallic state and have two $6s$ electrons and one $5d$ electron, while Eu has only two $6s$ electrons. In the atomic state Eu and Tb are divalent. We assume, as we have done earlier,[13] that the excitation processes in the atomiclike state at coverages below $\phi_{\min}$ or in the topmost layer of thick films are similar to those in free atoms. For the condensed state we compare our results with x-ray photoemission spectroscopy (XPS) data.

II. EXPERIMENTAL PROCEDURE

The experimental conditions were the same as those described in Refs. 13 and 14. The energy-loss spectra for Eu, Gd, and Tb deposited on the (110) and (211) faces of tungsten in UHV conditions (base pressure of 5×10^{-11} Torr) were investigated. The studies were preceded by a detailed analysis of various aspects of adsorption of these metals on the (110) and (211) faces of tungsten, which was presented in earlier papers.[15,16] The influence of coverage on loss energies and amplitudes was studied. The dependence on primary energy was investigated mainly with thick layers (about 100 ML). The experiments were performed using a cylindrical mirror analyzer (CMA) in the first derivative mode, with a modulation voltage of $0.5V_{pp}$. The primary energy range was 20–500 eV, the primary current ranged from a few tenths to a few μA. Particular attention was paid to the cleanness of the surface. The O:W and C:W Auger signal ratio did not exceed 1:100 and 1:300, respectively, during the measurements. Coverages (θ_s) are defined in units of the substrate atomic density.

III. RESULTS

Typical loss spectra of all the adsorbates in the energy region of the $5p$ excitation are presented in Fig. 1. These

0163-1829/93/47(24)/16506(7)/$06.00

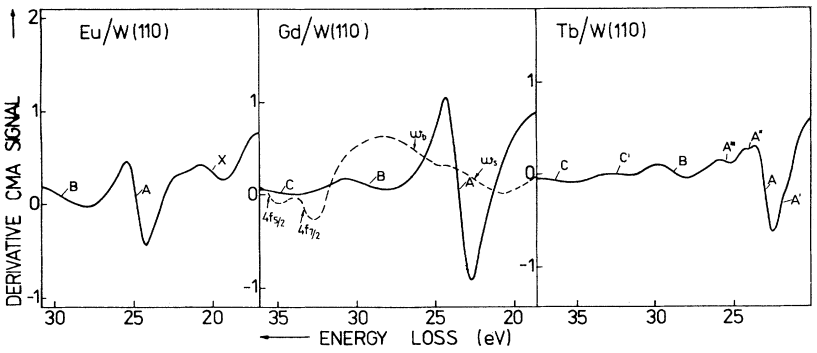

FIG. 1. Energy-loss spectra of thick layers in arbitrary units ($\gtrsim 100$ ML). $E_p = 80$ eV, modulation voltage 0.5 V_{pp}. The dashed line indicates clean W.

spectra are characteristic for thick layers (about 100 ML) at the relatively low primary energy $E_p = 80$ eV. Coverage changes influence not only the peak amplitudes but also the character of the spectra, which is especially clearly visible for Eu, as shown in Fig. 2. The Eu spectrum changes on both sides of the dominating loss A. The losses at energies of 32.5 and 34.5 eV are due to $4f$ electron excitation in tungsten. For the two other adsorbates the coverage influences only the high-energy side of the main loss but the detection of these changes is rather difficult due to their overlap with the tungsten $4f$ and plasmon losses.

The primary energy dependence of the loss spectra is shown for Gd in Fig. 3. With increasing E_p, new energy losses at energies 35 eV appear above 80 eV. Their amplitudes increase with primary energy and for $E_p > 400-500$ eV the loss with the highest energy (C) becomes predominant. This is clearly seen in Fig. 4 for Tb.

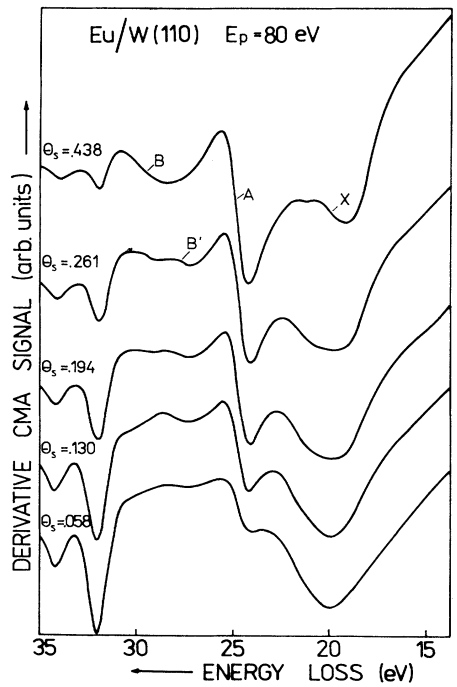

FIG. 2. Changes of the loss spectrum with Eu coverage. $E_p = 92$ eV, modulation voltage 0.5 V_{pp}.

The dependence of the loss amplitudes on the coverages is presented in Figs. 5–7. Figure 5 shows the results for Eu layers on the W(110) and W(211) faces. In both cases a new loss (X) appears at the minimum of the work function ($\theta_{min} = 0.3$ and 0.5 ML for the (110) and (211) faces, respectively). In all three elements the peak-to-peak height of the main loss (A) increases more slowly at coverages above the work-function minimum. The features C, in Gd as well as, C and C' in Tb overlap with the $4f$ excitation loss in tungsten. In Gd layers the loss position shifts continuously from the W $4f_{7/2}$ value (32.5 eV) to the Gd C value; in Tb layers the loss shown

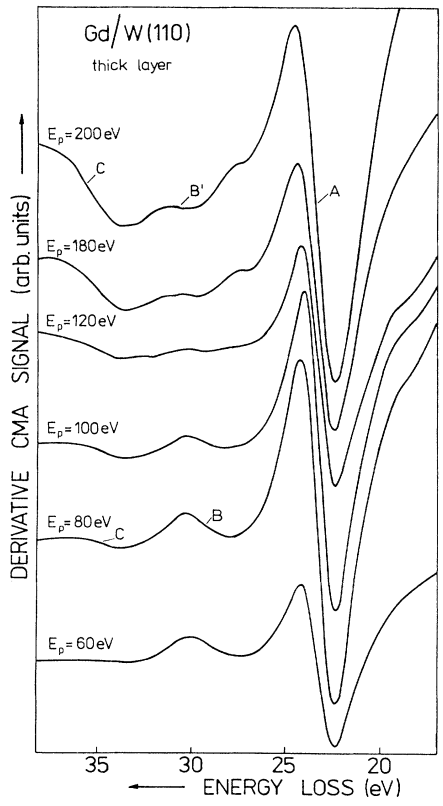

FIG. 3. Dependence of the loss spectrum of a thick Gd layer upon the primary electron energy. Plots corresponding to $E_p = 60$ and 80 eV were recorded with a modulation voltage of 1 V_{pp}, the others with 0.5 V_{pp}.

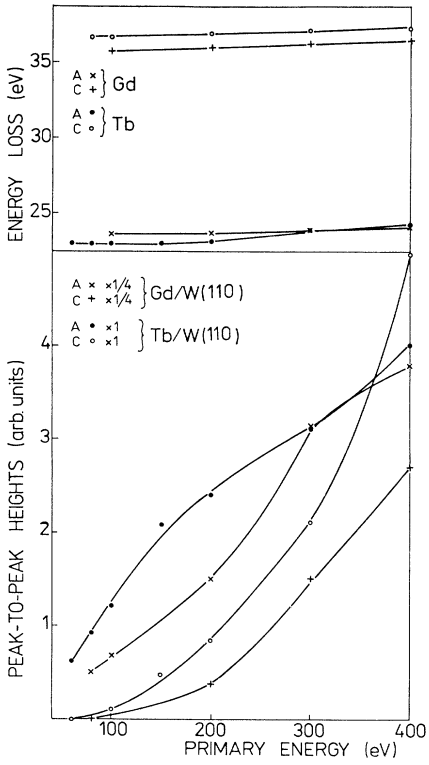

FIG. 4. Dependence of the main loss amplitudes (A and C) (bottom) and their energies (top) on E_p (thick layers).

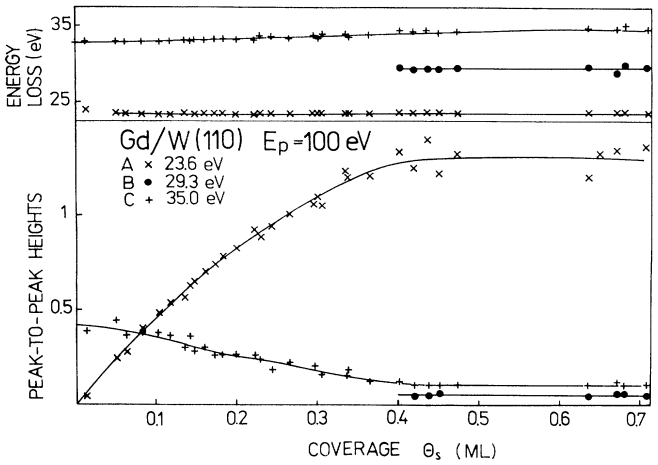

FIG. 6. Coverage dependences, in arbitrary units, of the loss amplitudes (bottom) and their energies (top) for Gd, monolayer completion at $\theta_s = 0.64$. $E_p = 100$ eV.

remains at the W $4f_{5/2}$ position up to $\theta_{\min}$ and then shifts rapidly to the Tb C loss position (not shown). In Gd layers the intensity of the W $4f_{7/2}$ peak decreases slowly until $\theta_{\min}$ while shifting in energy due to the overlap with the Gd C peak and then remains constant due to the growth of this peak. In Tb layers the intensity of the W

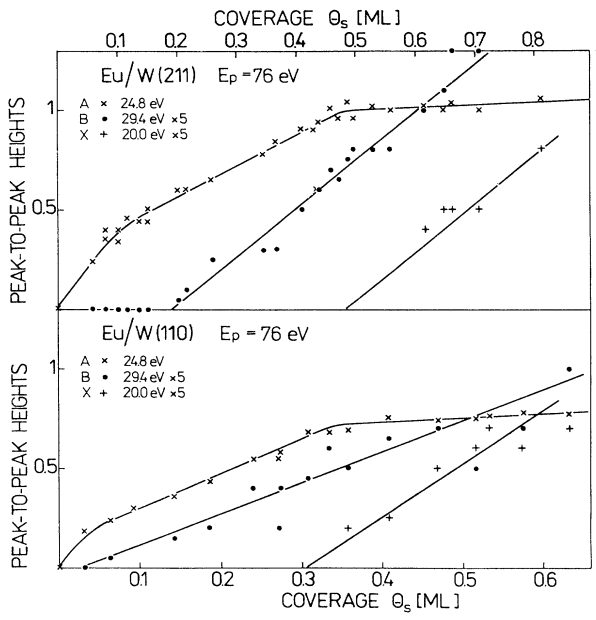

FIG. 5. Coverage dependence of the observed loss amplitudes for Eu/W(211) (monolayer completion at $\theta_s = 0.73$, top) and for Eu/(110) (monolayer completion at $\theta_s = 0.53$, bottom). In both cases $E_p = 76$ eV.

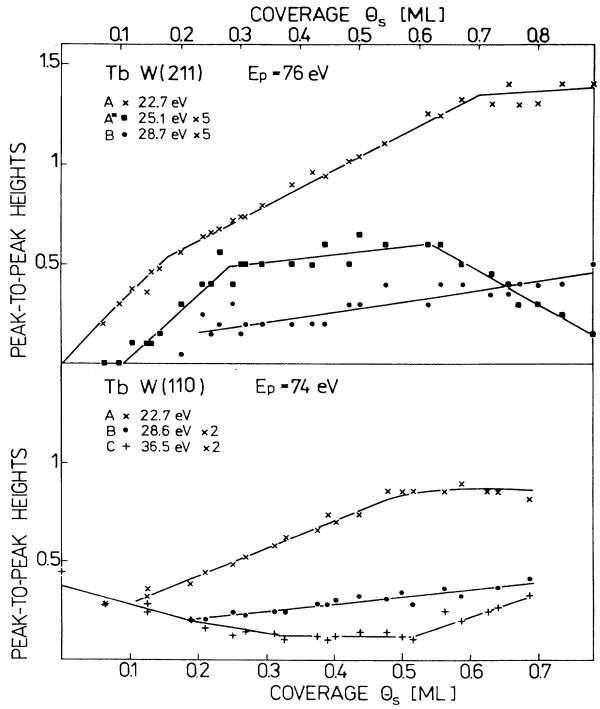

FIG. 7. Coverage dependence, in arbitrary units, of selected loss amplitudes for Tb/W(211) ($E_p = 76$ eV, monolayer completion at $\theta_s = 1.12$, top) and for Tb/W(110) ($E_p = 74$ eV, monolayer completion at $\theta_s = 0.64$, bottom).

TABLE I. Loss energies (in eV) for thick and thin layers of Eu, Gd, and Tb on W(110) and W(211) faces for various primary electron energies.

Eu	(110)		(211)		thick		oxygen contaminated	
E_p thick,80	76	76	76	30	150	thick,150	thin,92	
θ	0.07	0.24	0.35					
X 20.0				19.9	19.9	19.9	21.6	
A 24.8	24.8	24.8	24.8	24.8	24.8	24.8	24.8	
B'	27.9	27.9						
B 29.4		29.4	29.6		30.0	30.5	27.9	
						33.7		
Gd								
E_p 80	70	70		30	200	72		
θ	0.13	0.245						
A 23.6	23.6	23.6		23.5	23.6	23.6		
B 29.3					27.6	28.4		
C 35.0					35.5	36.2		
Tb	(110)		(211)					
E_p 80	74		76	30	200			
θ	0.25	0.13	0.365					
A' 21.9	21.9		21.5	21.9				
A 22.9	22.9	22.4	22.7	23.0	23.1			
A'' 24.1	24.1		23.7	24.1				
A''' 25.5	25.6	24.8	25.1		25.4			
B 28.8	28.6		28.7		28.0			
C' 32.5					32.0			
C 36.5					36.8			

$4f_{5/2}$ peak decreases until θ_{min} and then rises due to the formation of the Tb C loss. Peak B in Gd layers becomes detectable only above θ_{min}. All the identified losses and their energy values are collected in Table I for both thin and thick layers.

The influence of oxygen contamination on Eu and Gd layers was also studied. Typical spectra for such layers are shown in Fig. 3 in Ref. 13. Oxidation does not change the energy of loss A but causes clear changes in the overall shape of the spectra (Table I).

Losses due to 5s electron excitation in thick layers of all three elements were also measured. The 5s excitation cross sections are an order of magnitude smaller than those of the 5p level, and at small coverage no changes are detectable. The results are shown in Table II, together with data from the literature.

IV. DISCUSSION

A. 5s excitations

The presence of two 5s losses is due to the interaction between the single final-state 5s electron and electrons from unfilled shells (in this case mainly from the 4f

TABLE II. Binding energies of 5s and 5p and positions of unoccupied 4f- and 5d-state electrons (in eV) referred to the Fermi level.

	Eu	Gd	Tb
$5p_{3/2}$	24.8	23.6	22.9
$5p_{3/2}$	19.5 (Ref. 7); 18.9 (Ref. 19); 19 (Ref. 33)	22.8 (Ref. 7); 21.4 (Refs. 19 and 29); 20.4 (Ref. 32) 22 (Ref. 33)	25.6 (Ref. 7); 22.5 (Ref. 29) 22.6 (Ref. 32)
$5p_{1/2}$	29.4	29.3	28.8
$5p_{1/2}$	24.5 (Ref. 19)	27.7 (Refs. 19 and 29); 26.8 (Ref. 32)	28.5 (Ref. 29); 28.7 (Ref. 32)
5p splitting	4.6	5.7	5.9
	5.6 (Ref. 19)	6.6 (Ref. 19)	6.3 (Ref. 29)
5s	40.4; 44.2	46.6; 50.6	51.6; 54.7
5s	38.7 (Ref. 19); 45 (Ref. 31)	43.1 (Ref. 19); 46 (Ref. 31); 43 (Ref. 29)	48 (Ref. 31); 45 (Ref. 29)
5s splitting	3.8	4.0	3.1
	3.9 (Ref. 21); 3.8 (Ref. 17)	4.0 (Ref. 21); 3.6 (Ref. 17)	3.2 (Ref. 17)
4f	4 (Ref. 27); 8 (Refs. 23 and 26)	0 (Ref. 24); 4 (Ref. 28); 4 (Refs. 26 and 27)	0 (Ref. 25)
5d	4.3 (Refs. 26 and 27)	0 (Ref. 24)	

shell).[17] The observed splitting of the peaks, 3.8, 4.0, and 3.1 for Eu, Gd, and Tb, respectively, is identical to the splitting of the binding energies of the electrons emitted from the 5*s* level, as obtained with XPS (Refs. 18 and 19) (see Table II). However, the absolute values of the binding energies determined with XPS differ from the loss energies obtained with EELS. The differences between the loss energies and the binding energies, $\Delta E = E_L - E_B$, are 1.7, 3.5, and 3.6 eV for Eu, Gd, and Tb, respectively. The difference between Eu on the one hand and Gd and Tb on the other may be due to the different 5*d* occupation. The same 5*s* emission splitting, 3.9 eV for Eu (Refs. 20 and 21) and 4.2 eV for Gd,[21] was observed in the gas phase.

B. 5*p* excitations

If dipole selection rules are obeyed, the 5*p* electron may be excited to empty *d* or *s* states. In our case the 6*s* states are probably occupied, so that 5*p* excitations can occur only to 5*d* states which are empty in Eu or occupied with one electron in Gd and Tb. The *A* loss which is predominant in this energy region is due to the transition to the 5*d* level, because only levels with the same main quantum number and, therefore, a large wave-function overlap, show strong resonance effects.[6,22] However, the optically forbidden transition from the 5*p* to unoccupied 4*f* states cannot be excluded *a priori*. The difference $\Delta E = E_L - E_B$ between loss energy and binding energy is now different for all three elements: 5.9, 2.2 eV and 0.3 eV for Eu, Gd, and Tb, respectively (compare the losses *A* in Table I with the $5p_{3/2}$ binding energies of Refs. 19 and 29 in Table II). An unequivocal decision between the 4*f* and 5*d* transitions cannot be made on the basis of existing energy-level data. Absolute energy values from band-structure calculations[23–25] are not accurate enough to be used in a comparison between difficult materials. Experimental data are available from inverse-photoemission spectroscopy[26,27] and photoemission spectroscopy.[28] They give the following values of the 4*f* and 5*d* positions: $E_{4f} = 8$ eV (Refs. 26 and 27) for Eu and $E_{4f} = 4$ eV (Refs. 26 and 27) or 4.9 eV (Ref. 28) for Gd, $E_{5d} = 4.3$ eV (Ref. 27) for Eu and $E_{5d} = 0$ (Refs. 27 and 28) for Gd, all energies being referred to E_F. Thus, the difference $\Delta E = E_{4f} - E_{5d}$ is approximately the same for the two elements and the ΔE values cannot be used to distinguish between transition to 4*f* and to 5*d* states. A hint at a 4*f* transition is given by the comparison of the amplitude and structure of the *A* peaks of Gd and Tb, which is very reminiscent of the 4*f* multiplet structure of the XPS spectra of the two materials.[17] Therefore, at least at low energies, E_p, at which dipole selection rules are irrelevant, a $5p \rightarrow 4f$ excitation interpretation of loss *A* appears plausible. This interpretation cannot, however, explain the absence of the $5p^5 4f^{n+1} \rightarrow 5p^6 4f^{n-1} + e$ Auger deexcitation process in Eu.[2] This suggests that in Eu the loss *A* is not due to an excitation to the 4*f* level but rather to the 5*d* level. From the $5p^5 5d^1$ configuration of the excited Eu, no deexcitation with electron emission is possible. On the other hand, the $5p^2 5d^2$ configuration of excited Gd and Tb allows the process $5p^5 5d^2 \rightarrow 5p^6 + e$, and electrons of proper energies have actually been recorded in the emission spectra of those elements.[2]

Loss *B* is separated from loss *A* by 4.6, 5.7, and 5.9 eV for Eu, Gd, and Tb, respectively, which corresponds approximately to the binding-energy differences of the $5p_{3/2}$ and $5p_{1/2}$ levels, 5.6, 6.3, and 6.1 eV, respectively (Table II).[19,29] The initial state of this loss is accordingly the $5p_{1/2}$ level, and the final state, as in loss *A*, is the 5*d* level (or possibly the 4*f* level at low excitation energies). The remaining losses will be discussed separately for the various materials.

1. *Eu*

For Eu a new feature *X* at 20.0 eV appears in the loss spectrum above $\phi_{\min}$. This loss may be related to a partially empty $(6s6p)^2$ band near the E_F in the 2*d* crystal which forms above $\phi_{\min}$, as seen in the accompanying structural changes.[15,16] This interpretation is supported by the energy of loss *X*, which is 4.8 eV lower than that of loss *A*. Loss *A* had been attributed above to a $5p \rightarrow 5d$ (or at low energies to a $5p \rightarrow 4f$) excitation and the 5*d* level was placed 4.3 eV above E_F. Moreover, the increase of the loss *A* with increasing coverage (Fig. 5) slows down when loss *X* appears, which is evidence for competing excitation processes, $5p \rightarrow 5d(4f)$ and $5p \rightarrow (6s6p)^2$.

The weak loss *B'* is visible only at low coverages (Fig. 2) and is, therefore, interpreted as a transition to an empty 4*f* atomiclike state. The 5*p* binding energies of Eu in the atomic state, 32.5 and 26.7 eV are 8 eV larger than those in the metallic state, 24.5 and 18.9 eV.[19] The energy of loss *B'* which disappears at $\phi_{\min}$ is 7.9 eV larger than that of loss *X* (Table II, and Fig. 2) which appears at $\phi_{\min}$. Therefore, loss *B'* in the atomiclike state of the layer is attributed to a similar excitation as loss *X* is in its metallic state; that is, to a $5p \rightarrow 6p$ transition.

2. *Gd*

The high-energy loss *C* is seen only at energies $E_p > 80$ eV and increases rapidly with energy, finally dominating this loss region at the expense of loss *A* (Figs. 3 and 4). Loss *C* (35.5 eV) appears only at higher primary energies E_p. It is attributed to a two-electron process involving a $5p \rightarrow 5d$ transition and a transition from the 5*d* level to continuum states ε with a high density of states because it is absent in Eu, which has no 5*d* electron. The $5p \rightarrow 5d$ excitation which causes loss *A* requires an energy of 23.6 eV (Table I), which leaves 11.9 eV for the $5d \rightarrow \varepsilon$ excitation. Taking the work function of the analyzer (≈ 5 eV) into account, emitted electrons are expected with an energy of 6.9 eV. Electrons with 7.0-eV energy have indeed been detected in the secondary-electron spectrum.[2] A bulk plasmon excitation would require an energy of 13.3 eV (Ref. 13) and is, therefore, excluded as a simultaneous excitation process. Also, the loss energy shifts with increasing Gd coverage from the W 4*f* value (32.5 eV) continuously towards the value found in thick Gd layers (Fig. 6), indicating the existence of loss *C* already below $\phi_{\min}$, which is in the atomiclike state, in which no plasmon excitation is possible.

At the primary energies at which loss C becomes clearly visible, that is, at $E_p \sim 100$ eV (Fig. 4), loss B ($5p_{1/2} \rightarrow 5d$) is replaced by some less-pronounced features (Fig. 3), which, by analogy to loss C, are assigned to two-electron excitations overlapping with loss B. Because of this overlap, no analysis of this part of the spectrum is possible. The emission probably also involves $6s$ electrons. This is suggested by a comparison of oxygen-contaminated and clean layers. Measurements at $E_p = 72$ eV show that loss C is much weaker in the oxidized state. The loss height ratios $C:A$ are 1:11.4 and 1:5.5 for oxygen-contaminated and clean surfaces, respectively. Oxidation causes a valence-electron transfer from metal to oxygen, so that the emission accompanying the $5p$ excitation is less probable. In Eu the B loss disappears completely upon oxidation, which shows that the $6s$ electrons are necessary for this feature in the $5p$ loss spectrum.

3. Tb

The terbium spectrum (Fig. 1) shows, in addition to losses A, B, and C, which are also seen in Gd, several less-intense features (A', A'', A''', C'). The losses $A' - A'''$ are best seen in the films below $\phi_{\min}$, in particular on the (211) surface, in thick films at low primary energies ($E_p \sim 50$ eV). Therefore, they are assigned to atomiclike transitions in the topmost layer. In the atomic state the lowest levels of Tb have configurations $4f^8 5d 6s^2$ and $4f^9 6s^2$, which are separated by only 0.035 eV.[30] In the energy range up to 5.5 eV there are many transitions from these states to excited states involving changes in the occupation of the $4f$, $5d$, and $6s$ levels.[30] If the $5p \rightarrow 5d$ excitation is accompanied by one of these excitations, a large number of closely spaced losses is possible, so that a reliable assignment is not possible. The observation that in Gd (the $4f^7$ configuration) no satellites of loss A are observed suggests that the occupation of the $4f$ level in Tb (the $4f^8$ or $4f^9$ configuration) plays an important role for the probability of the excitations which cause the losses $A' - A'''$ in the atomiclike state.

Loss C is of the same nature as loss C in Gd, which is due to a two-electron excitation $5p \rightarrow 5d, 5d \rightarrow \varepsilon$ into the continuum. The energy difference between loss C and loss A, 13.7 eV, is approximately equal to the volume plasmon loss 13.5 eV,[13] and loss C is observed only above $\phi_{\min}$, which is in the two-dimensional condensed state. Therefore, plasmon excitation simultaneous with $5p \rightarrow 5d$ excitation cannot be excluded. However, electrons with approximately the correct energy for the $5p \rightarrow 5d, 5d \rightarrow \varepsilon$ transition are found in the emission spectrum.[2] Loss C' is tentatively assigned to a two-electron excitation $5p \rightarrow 5d, 4f \rightarrow 5d$.

V. CONCLUSIONS

The loss spectra of Eu, Gd, and Tb depend strongly upon coverage. This is due to the change of the electronic structure of the adsorption layer with coverage. The results presented also show that even at very low coverages the $6s$ electrons are not transferred to the substrate because no losses due to $5p \rightarrow 6s$ excitation were observed. Therefore, the layer is not ionic but consists of strongly polarized atoms.

Our results refute the widely accepted picture that plasmon losses make a large contribution to the energy-loss spectrum in the valence region as well as in the $5p$ region.[7] The plasmon losses have energies of 7.8, 13.3, and 13.5 eV for Eu, Gd, and Tb, respectively.[13] Multiple plasmon losses should occur at 15.6, 26.6, and 27 eV, but such losses were not observed here even at the highest primary energies. For the 29.4-eV loss in Eu and the 35-eV loss in Gd, plasmon excitation simultaneous with $5p \rightarrow 5d$ excitation can be excluded as a possible cause, also in conjunction with a $5p \rightarrow 5d$ excitation; in Tb such a simultaneous excitation, however, can possibly cause the 36.5-eV loss.

ACKNOWLEDGMENTS

The experiments were carried out with support by the Deutsche Forschungsgemeinschaft. Partial support by the State Committee of Scientific Research (KBN) Grant No. 2011199101 is also acknowledged.

[1] F. P. Netzer and J. A. D. Matthew, Rep. Prog. Phys. **49**, 621 (1986).
[2] J. Kołaczkiewicz and E. Bauer, Surf. Sci. **273**, 109 (1992).
[3] F. Gerken, J. Barth, K. L. I. Kobayashi, and C. Kunz, Solid State Commun. **35**, 179 (1980).
[4] F. P. Netzer, E. Bertel, and J. A. D. Matthew, J. Phys. C **14**, 1981 (1981).
[5] S. Modesti, G. Paolucci, and E. Tosatti, Phys. Rev. Lett. **55**, 2995 (1985).
[6] F. Gerken, J. Barth, and C. Kunz, Phys. Rev. Lett. **47**, 993 (1981).
[7] F. P. Netzer, G. Strasser, G. Rosina, and J. A. D. Matthew, J. Phys. F **15**, 753 (1985).
[8] J. P. Gaspar, A. G. Eguiluz, K.-D. Tsuei, and E. W. Plummer, Phys. Rev. Lett. **67**, 2854 (1991).
[9] B. Woratschek, W. Sesselmann, J. Küppers, G. Ertl, and H. Haberland, Phys. Rev. Lett. **55**, 1231 (1985).
[10] G. M. Lamble, R. S. Brooks, D. A. King, and D. Norman, Phys. Rev. Lett. **61**, 1112 (1988).
[11] D. M. Riffe, G. K. Wertheim, and P. H. Citrin, Phys. Rev. Lett. **64**, 571 (1990).
[12] H. Ishida and K. Tarakura, Phys. Rev. B **38**, 5752 (1988).
[13] J. Kołaczkiewicz and E. Bauer, Surf. Sci. **265**, 39 (1992).
[14] E. Bauer and J. Kołaczkiewicz, Phys. Status Solidi B **131**, 699 (1985).
[15] J. Kołaczkiewicz and E. Bauer, Surf. Sci. **175**, 487 (1986).
[16] J. Kołaczkiewicz and E. Bauer, Surf. Sci. **154**, 357 (1985).
[17] M. Campagna, G. K. Wertheim, and Y. Baer, in *Photoemission in Solids II*, edited by L. Ley and M. Cardona, Topics in Applied Physics Vol. 27 (Springer, Berlin, 1979).

[18]F. R. MacFeely, S. P. Kowalczyk, L. Ley, and D. A. Shirley, Phys. Lett. **49A**, 301 (1974).
[19]M. Richter, T. Prescher, M. Meyer, E. v. Raven, B. Sonntag, H.-E. Wetzel, and S. Aksala, Phys. Rev. B **38**, 1763 (1988).
[20]U. Becker, H. G. Kerkhoff, D. W. Lindle, P. H. Kobrin, T. A. Ferrett, P. A. Heimann, C. M. Truesdale, and D. A. Shirley, Phys. Rev. A **34**, 2858 (1986).
[21]M. Richter, M. Meyer, M. Pahler, T. Prescher, E. v. Raven, B. Sonntag, and H.-E. Wetzel, Phys. Rev. A **40**, 7007 (1989).
[22]W. F. Egelhoff, Jr., G. G. Tibbetts, M. H. Hecht, and L. Lindau, Phys. Rev. Lett. **46**, 1071 (1981).
[23]B. I. Min, H. J. F. Jansen, T. Oguchi, and A. J. Freeman, J. Magn. Magn. Mater. **59**, 277 (1986).
[24]J. Sticht and J. Kübler, Solid State Commun. **53**, 529 (1985).
[25]S. C. Wu, H. Li, D. Tian, J. Quinn, Y. S. Li, F. Jona, J. Sokolov, and N. E. Christensen Phys. Rev. B **41**, 11 911 (1990).
[26]J. K. Lang, Y. Baer, and P. A. Cox, J. Phys. F **11**, 121 (1981).
[27]R. Hofmann and F. P. Netzer, Phys. Rev. B **43**, 9720 (1991).
[28]F. J. Himpsel and B. Reihl, Phys. Rev. B **28**, 574 (1983).
[29]F. Gerken, Ph.D. thesis, University of Hamburg, 1979.
[30]*Gmelin Handbuch der Anorganischen Chemie,* edited by G. Kirschstein (Springer, Berlin, 1976), Vol. 39B4, p. 218–262.
[31]*Handbook of X-Ray and Ultraviolet Photodetection Spectroscopy,* edited by D. Briggs (Heyden and Son, London, 1977).
[32]C. S. Fadley, in *Electron Spectroscopy: Theory, Techniques and Applications,* edited by C. R. Brundle and A. D. Baker (Academic, New York, 1978).
[33]P. O. Heden, H. Lofgren, and S. B. M. Hagstrom, Phys. Status Solidi B **49**, 721 (1972).