PHYSICAL REVIEW B VOLUME 20, NUMBER 6 15 SEPTEMBER 1979

Bulk- and surface-plasmon-loss intensities in photoelectron, Auger, and electron-energy-loss spectra of Mg metal

P. M. Th. M. van Attekum and J. M. Trooster
Department of Physical Chemistry, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

(Received 12 February 1979)

The intensities of plasmon-loss satellites in x-ray photoelectron (XPS) and electron-energy-loss (EEL) spectra of Mg metal have been determined. The method used has been described earlier in a similar study of aluminum. Intrinsic processes contribute 22% of the total plasmon intensity in the case of XPS core lines. The probability for extrinsic plasmon excitations is $\alpha = 0.67$, in good agreement with the value $\alpha = 0.63$ derived from the EEL spectra with primary-electron energies ranging from 300 to 1500 eV. For *KLL* and *KLV* Auger lines we find the same contributions of intrinsic and extrinsic processes to the plasmon intensities as for the XPS core lines. The line shapes of plasmon-loss lines are different in XPS and EEL spectra, and cannot be described as self-convolutions of the plasmon-energy distribution function.

I. INTRODUCTION

Following our investigation of plasmon losses in x-ray-photoelectron (XPS), Auger, and electron-energy-loss (EEL) spectra of aluminum,[1] we report here on a similar study of magnesium metal.

The method used to determine the intensities of the plasmon-loss lines has been extensively described in Ref. 1. Here we reiterate the most important features.

(a) The *n*th bulk-plasmon-loss line, P_n, is calculated as a convolution of the measured no-loss line, $P_0(E)$, with a plasmon-loss energy distribution function $D_n(E)$

$$P_n(E) = P_0(E) * D_n(E) . \tag{1}$$

(b) The plasmon-loss energy distribution function $D_n(E)$ is given by an asymmetric Lorentzian

$$D_n(E) = \frac{I_n}{\left[1 + \left(\frac{E - E_n}{\Gamma_n(E)}\right)^2\right]} , \tag{2}$$

where $E_n = nE_B$, with E_B the bulk-plasmon energy, $\Gamma_n(E) = n\Gamma^R$ for $E < E_n$, and $\Gamma_n(E) = n\Gamma^L$ for $E > E_n$.

(c) Similar expressions are used for the surface-plasmon-loss line and for lines due to loss of one surface-plasmon loss and one or more bulk-plasmon losses. Altogether this results in the following parameters: E_B, E_S, Γ^R, Γ^L, Γ_S^R, Γ_S^L, I_n, and I_S.

The experiments were carried out on a Leybold-Heraeus LHS-10 spectrometer. XPS spectra were measured with Mg $K\alpha$ radiation and Auger spectra were measured with Al $K\alpha$ radiation. The EEL spectra were measured with primary electron energies ranging from 300 to 1500 eV. The energy width of the primary electrons was 0.5 eV.

II. ANALYSIS AND RESULTS

A. XPS core lines and valence band

Figure 1(a) presents a typical photoelectron spectrum, excited with Mg $K\alpha$ radiation, used in the analysis. To obtain a high count rate the electron-energy analyzer was set for a pass energy of 150 eV, resulting in an instrumental resolution of 1.0 eV. The *KLL* and *KLV* Auger lines, which are present in the experimentally measured spectrum because of the Bremsstrahlung background from the x-ray source, were subtracted using the Auger spectrum measured with Al $K\alpha$ radiation given in Fig. 2(a). Lines due to x-ray satellites were removed with a procedure described elsewhere.[2] The binding energy of the 2*s* and 2*p* electrons is 88.6 ± 0.1 eV and 49.6 ± +0.1 eV, respectively, in good agreement with results of other authors.[3,4]

Starting from the right in the spectrum the plasmon-loss intensity is calculated for each data point and subtracted from the measured intensity (see Ref. 1 for a detailed description of this method). If the method was perfect the result should be the two no-loss core lines, each with Doniach-Sunjic line shape as discussed by Citrin *et al.*,[5] modified by the instrumental resolution. However, as in the case of Al,[1] it was necessary to allow for a constant background to the left of the core lines. A least-squares-fitting method[6] was used to determine the parameters given above, using seven bulk-plasmon-loss lines for each XPS line. The parameter values are listed in Table I. The values of E_B and E_S are in good agreement with results of Ley *et al.*[3] and 0.1–0.2 eV lower than found by Fuggle *et al.*[4,7] and Tejada *et al.*[8] The ratio $E_B/E_S = 1.47$ is close to the theoretical value 1.41. The optimum result after removal of the plasmon-loss lines is shown in Fig.

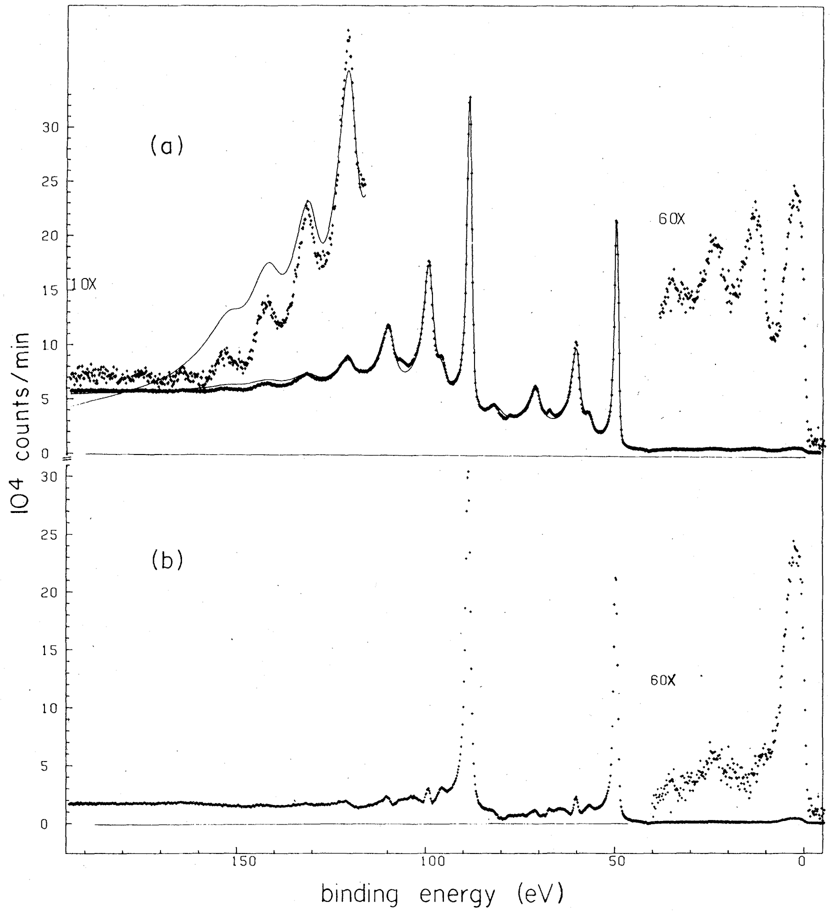

FIG. 1. (a) Photoemission spectrum of the 2s and 2p core levels and valence band of Mg metal after removal of the Auger lines and x-ray satellites. The solid line is the calculated spectrum (see text). (b) After the removal of the plasmon-loss lines using the parameters of Table I.

1(b). A reasonable fit could be obtained only up to the third plasmon-loss line. This is most clearly apparent in Fig. 1(a), where the spectrum is calculated as a convolution of $D_n(E)$ with the no-loss spectrum obtained from Fig. 1(b) by smoothing. For higher-order plasmon-losses the constraints used in the fit result in too large linewidths. The measured linewidths of the higher-order plasmon losses are also much smaller than one would expect if the line shapes were given by self-convolutions of the first plasmon-loss energy distribution function. The same result was obtained for plasmon losses in aluminum, but is more pronounced in the present case. An attempt to fit the spectrum with independent linewidths did not result in an appreciable improvement.

In our method the area intensities A_n of the successive plasmon-loss lines are directly obtained as fraction of the area intensity of the no-loss line, without actually determining the line shape and intensity of this no-loss line. The probability for extrinsic and intrinsic plasmon excitation can be derived using the expression[9,10]

$$A_n = \alpha^n \sum_{m=0}^{n} \frac{(\beta/\alpha)^m}{m!}, \tag{3}$$

where the probability for extrinsic plasmon excitation $\alpha = (1 + l/L)^{-1}$, l is the mean free path for extrinsic plasmon excitation, L is the mean attenuation length for electrons due to processes other than plasmon excitation. The parameter β is a measure of the probability of intrinsic excitation of plasmons modified by interference effects between intrinsic and extrinsic plasmon excitations. From the first three experimental area intensities A_1, A_2, and A_3, we find $\alpha = 0.67 \pm 0.05$ and $\beta = 0.19 \pm 0.05$. In Table II the measured and calculated values of A_n are given. Note that with these values the total intensity for bulk-plasmon excitation is about two times the intensity in the no-loss line and that the contribution of intrinsic processes is about 22% of the total plasmon intensity.

TABLE I. Best parameter values for the plasmon losses in Mg metal. The peak intensity (I_n, I_S) is given in percentage units of the no-loss peak per ΔE, where ΔE is the energy increment per channel. Errors are given in units of the last decimal.

parameter	value	units
E_B	10.63(5)	eV
E_S	7.23(5)	eV
Γ^L	1.07(5)	eV
Γ^R	0.65(5)	eV
Γ_S^L	1.25(5)	eV
Γ_S^R	0.70(5)	eV
I_1	31.3(5)	%eV^{-1}
I_2	11.5(3)	%eV^{-1}
I_3	4.5(2)	%eV^{-1}
I_4	2.2(2)	%eV^{-1}
I_5	1.3(2)	%eV^{-1}
I_6	0.6(1)	%eV^{-1}
I_7	0.3(1)	%eV^{-1}
I_S	5.8(2)	%eV^{-1}

TABLE II. Experimental area intensities of the bulk- and surface-plasmon losses compared with calculated values from Eq. (3). Experimental values in brackets are less reliable. The area intensity is listed in percentage units of the no-loss line and given by $A_n = \frac{1}{2}\pi(\Gamma_n^L + \Gamma_n^R) I_n$ (see Table I). The errors are estimates based on several fits.

parameter	experiment (%)	theory (%) $\alpha = 0.67, \beta = 0.19$
A_1	84 ± 3	86
A_2	62 ± 3	60
A_3	37 ± 3	40
A_4	(24)	27
A_5	(17)	18
A_6	(10)	12
A_7	(6)	8
A_S	18 ± 3	. . .

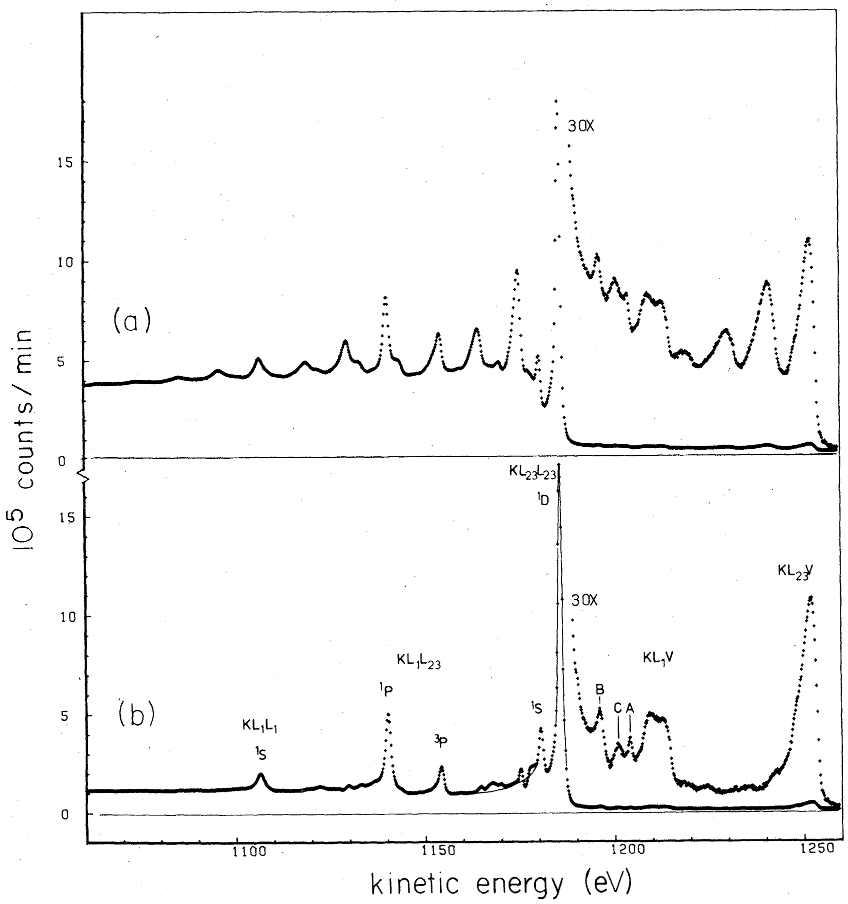

FIG. 2. X-ray-excited (Al$K\alpha$) KLL and KLV Auger spectrum of Mg metal. The kinetic energy scale is corrected for the work function. (a) As measured. (b) After removal of the plasmon-loss lines using the parameters of Table I. A is the internal-photoemission Mg $2p$ line, B a plasmon-gain of the $KL_{2,3}L_{2,3}$ (^1D) Auger line, C a small carbon impurity.

TABLE III. Kinetic energies (in eV), corrected for the work function, of the *KLL* and *KLV* Auger lines in Mg metal. Errors are given in units of the last decimal.

peak	this work	Fuggle *et al.* (Ref. 7) (experiment)	Ley *et al.* (Ref. 3) (experiment)	Hoogewijs (Ref. 12) (theory)
KL_1L_1 (^1S)	1106.4(2)	1106.2(2)	1106.0(3)	1109.3
$KL_1L_{2,3}$ (^1P)	1140.2(2)	1140.1(1)	1139.8(2)	1141.3
$KL_1L_{2,3}$ (^3P)	1154.2(2)	1154.1(3)	1154.3(6)	1155.8
$KL_{2,3}L_{2,3}$ (^1S)	1180.5(2)	1180.5(1)	1179.8(2)	1180.4
$KL_{2,3}L_{2,3}$ (^1D)	1185.9(2)	1185.5(1)	1185.3(2)	1186.4
$KL_{2,3}L_{2,3}$ (^3P)	...	...	...	1190.4
KL_1M_1	1209.5(3)	1208.8(5)	...	...
$KL_1M_{2,3}$	1212.6(3)	1212.8(5)	...	...
$KL_{2,3}M_1$				
$KL_{2,3}M_{2,3}$	1251.9(2)	1251.7(4)	...	...

The valence-band spectrum is of similar shape as found by Ley *et al.*[3] and Höchst *et al.*[11] The small increase in intensity at 24 eV binding energy is possibly due to a small oxygen impurity, O(2*s*). This precludes any determination of β for the valence band. In the case of Al we found β to be smaller for the valence band.

B. Auger spectrum

In Fig. 2 the *KLL* and *KLV* Auger spectrum of Mg metal in shown. Table III lists the values for the kinetic energies corrected for the work function, together with experimental data of Fuggle *et al.*[7] and Ley *et al.*,[3] and with theoretical results of Hoogewijs *et al.*[12] There is good agreement with theoretical values.

In Fig. 2(b) we show the same spectrum after subtraction of the plasmon-loss lines using the parameters in Table I. Both for the *KLL* and *KLV* transitions the deviations from a smooth line are similar magnitude and shape as for the 2*s* and 2*p* XPS core lines [Fig. 1(b)]. This implies, that the intrinsic plasmon intensity is the same for the Auger and XPS lines. A similar conslusion was obtained for Al.[1]

The small peaks labeled *A*, *B*, and *C* are due to internal photoemission from the 2*p* core level (*A*), a plasmon-gain satellite of the $KL_{2,3}L_{2,3}$ (^1D) Auger transition (*B*), and a small carbon impurity (*C*), and have been discussed elsewhere.[13] It has to be noted that since low-intensity x-rays were used as exciting radiation, peak *B* cannot be due to double ionization. The occurrence of the plasmon-gain satellite confirms the importance of intrinsic plasmon excitations.

C. Electron-energy-loss spectra

In EEL spectra intrinsic processes cannot occur and hence the area ratio of successive plasmon-loss lines should be equal to α, the probability for extrinsic

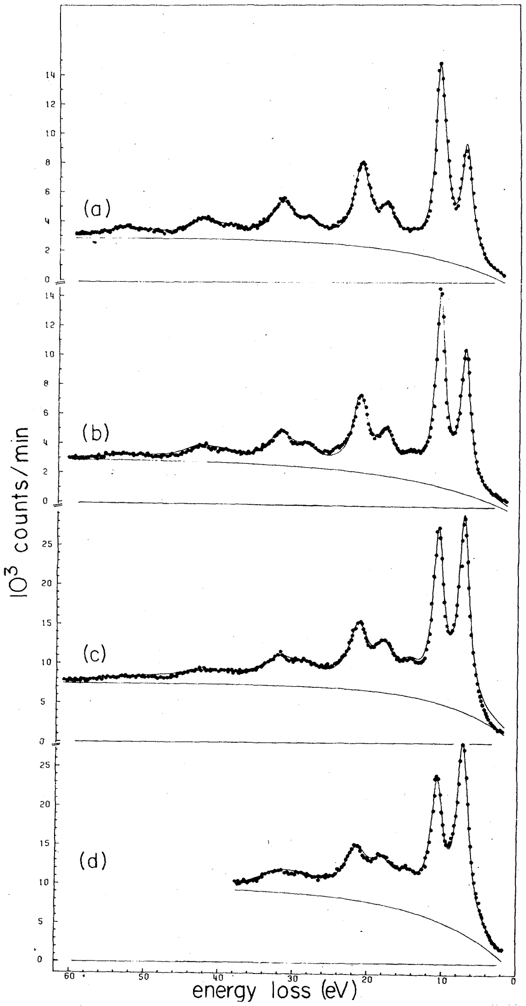

FIG. 3. Electron-energy-loss spectra of Mg metal (points) fitted with symmetrical Lorentzians at different values of the primary energy (E_0). The baseline is indicated with a solid line. (a) $E_0=1505$ eV. (b) $E_0=1008$ eV. (c) $E_0=499$ eV. (d) $E_0=336$ eV.

TABLE IV. Best parameter values for the plasmon losses in the EEL spectra of Mg metal as function of the primary energy E_0. E_B and E_S are the bulk and surface plasmon energy, I_1, I_S and I_S^2 are the peak heights of the first bulk-plasmon loss, and the first and second surface-plasmon loss, respectively. $R = I_{S,n-1}/I_n$ for $n > 1$, $\alpha = I_{n+1}/I_n$, where I_n is the intensity of a peak corresponding with n bulk-plasmon losses, $I_{S,n}$ the intensity corresponding to n bulk-plasmon losses and one surface-plasmon loss. Γ is the linewidth and a, b, and c are the baseline parameters. Errors are estimates based on several fits and given in units of the last decimal.

	$E_0 = 336$ eV	$E_0 = 499$ eV	$E_0 = 1008$ eV	$E_0 = 1505$ eV
E_B (eV)	10.8(1)	10.7(1)	10.7(1)	10.7(1)
E_S (eV)	7.3(1)	7.3(1)	7.3(1)	7.2(1)
I_S/I_1	1.47(5)	1.17(5)	0.74(5)	0.60(5)
R	0.70(5)	0.62(5)	0.49(5)	0.40(5)
I_S^2/I_1	0.36(5)	0.26(5)	0.18(5)	0.05(5)
α	0.65(2)	0.63(2)	0.61(2)	0.62(2)
Γ_1 (eV)	2.0(1)	1.7(1)	1.6(1)	1.8(1)
Γ_2 (eV)	3.8(1)	3.1(1)	2.5(1)	2.6(1)
Γ_3 (eV)	6.9(2)	5.5(2)	3.7(2)	3.7(2)
Γ_4 (eV)	⋯	10.9(3)	5.4(3)	5.0(3)
Γ_5 (eV)	⋯	15.0(5)	14.6(3)	6.0(3)
a	1.11(3)	1.03(3)	1.28(3)	1.30(3)
c (eV)	10.9(2)	8.9(2)	14.4(2)	12.3(2)
I_1/b	5.0(1)	7.3(1)	10.4(1)	12.0(1)

plasmon excitation [see Eq. (3)]. The primary energy E_0 was varied from 300 to 1500 eV and the dependence of α on the primary energy was examined. Figure 3 gives the EEL spectra of Mg metal at primary energies of 336, 499, 1008, and 1505 eV. Note the increase in surface-plasmon intensity going to lower primary energies and the presence of a peak due to the excitation of two surface plasmons. This peak occurs as the scattered electron crosses the surface twice. The intensity analysis is hampered by a background which increases with increasing energy loss. As in the case of Al metal[1] the plasmon-loss lines could be described with symmetrical Lorentzians. The background was approximated by $B(E) = b\{1 - a\exp[-(E - E_0)/c]\}$. In fitting the spectra the same constraints were used as in Ref. 1. The most important features are: Within each pair of bulk- and surface-plasmon-loss lines, the linewidth was kept equal. Similarly the intensity ratio within each pair was kept constant except for the first pair. The area intensity ratio of successive bulk-plasmon-loss lines was set equal to α. The fits are shown in Fig. 3 and the parameters are tabulated in Table IV. The following points should be noted: (a) The value of α is constant in the primary energy range studied and has the value 0.63 ± 0.04, in good agreement with the value determined for the XPS core lines. (b) After subtraction of the linewidth of the no-loss line (0.5 eV) the linewidth of the first plasmon-loss line is markedly smaller than in the XPS spectra. (c) The linewidths increase with decreasing primary energy and with increasing order of the loss line. (d) The assumed shape of the baseline appears to be a good approximation. The ratio of the baseline intensity to the intensity of the first plasmon-loss line increases with decreasing primary energy. (e) The fact that the ratio of surface to bulk-plasmon intensity in the first pair is different from that in the second-and higher-order pairs indicates that an appreciable fraction of the electrons scatters from the surface without entering the (bulk) metal and has therefore none or little probability for exciting bulk plasmons as well. This fraction obviously increases with decreasing primary energy.

III. CONCLUSIONS

The results of this investigation are similar to those found on Al,[1] and are detailed below.

(a) Intrinsic plasmon excitations are important and contribute for XPS core lines about 22% to the total of the plasmon excitations. A similar result was found by Steiner *et al.*,[14] who gave, however, no details of the fitting procedure.

(b) For the *KLL* and *KLV* Auger lines the same parameter values as for the core lines are obtained. The occurrence of a plasmon-gain satellite of the $KL_{2,3}L_{2,3}$ (^1D) Auger line confirms the importance of intrinsic processes.

(c) Electron-energy-loss spectra for primary energies ranging from 300 to 1500 eV are analyzed with symmetrical Lorentzians. From this a value of $\alpha = 0.63$ is found, in good agreement with the value determined for the XPS core lines.

(d) The line shape of plasmon-loss lines depends on the energy of the primary electrons in EEL spectra and at the same primary energy is different for XPS and EEL spectra. Also, successive plasmon-loss lines cannot be described as self-convolutions of the plasmon-loss energy distribution function.

ACKNOWLEDGMENT

We gratefully acknowledge the technical assistance of Mr. A. E. M. Swolfs.

---

[1] P. M. Th. M. van Attekum and J. M. Trooster, Phys. Rev. B 18, 3872 (1978).

[2] P. M. Th. M. van Attekum and J. M. Trooster, J. Electron Spectrosc. Relat. Phenom. 11, 363 (1977).

[3] L. Ley F. R. McFeely, S. P. Kowalczyk, J. G. Jenkin, and D. A. Shirley, Phys. Rev. B 11, 600 (1975).

[4] J. C. Fuggle, Surf. Sci. 69, 581 (1977).

[5] P. H. Citrin, G. K. Wertheim, and Y. Baer, Phys. Rev. B 16, 4256 (1977).

[6] F. James and M. Roos, Comp. Phys. Commun. 10, 343 (1975).

[7] J. C. Fuggle, L. M. Watson, D. J. Fabian, and S. Affrossman, J. Phys. F 5, 375 (1975).

[8] J. Tejada, M. Cardona, N. J. Shevchik, D. W. Langer, and E. Schönherr, Phys. Status Solidi b 58, 189 (1973).

[9] D. Langreth, in *Collective Properties of Physical Systems*, edited by B. and S. Lundqvist (Academic, New York, 1974).

[10] W. J. Pardee, G. D. Mahan, D. E. Eastman, R. A. Pollak, L. Ley, F. R. McFeely, S. P. Kowalczyk, and D. A. Shirley, Phys. Rev. B 11, 3614 (1975).

[11] H. Höchst, P. Steiner and S. Hüfner, J. Phys. F 7, L309 (1977).

[12] R. Hoogewijs, L. Fiermans and J. Vennik, J. Electron Spectrosc. Relat. Phenom. 11, 171 (1977).

[13] P. M. Th. M. van Attekum and J. M. Trooster, J. Phys. F 8, L169 (1978).

[14] P. Steiner, H. Höchst, and S. Hüfner, Phys. Lett. A 61, 410 (1977).