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Core-hole-induced degeneracy of the valence subshells in the $5p$ photoemission of atomic europium

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The $5p$ photoemission spectrum of atomic europium has been analyzed using high-resolution photoelectron spectroscopy. In contrast to the expected simple multiplet structure of a $5p^{-1}4f^7(^8S)$ configuration with six main lines, the observed Eu $5p$ photoemission shows a very complex spectrum. Configuration-interaction calculations reveal that the $5p$ core hole gives rise to a near degeneracy of the valence subshells in the final ionic states, so that the main multiplet structure of the spectrum can only be described by a strong mixture of the configurations $6s^2$, $6s5d$, $5d^2$, and $6p^2$. This mixing also results in a strong broadening of the lines at higher binding energy.

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The great interest in magnetic systems such as magnetic multilayers or ultrathin films has prompted the use of numerous spectroscopic methods to study the electronic and magnetic structure of the transition metals (TM's) and the rare earths (RE's) in these materials. Among these methods core-level spectroscopy with modern techniques such as angle- and spin-resolved photoemission or magnetic dichroism is widely used. The interpretation of data in these experiments is intimately connected with the multiplet splitting caused by the interaction of the core hole with the $3d$ (TM) or $4f$ (RE) electrons. For the localized $4f$ (RE) electrons special interest is given to the electronic and magnetic properties of ferromagnetic gadolinium with its rather stable half-filled subshell $4f^7(^8S)$. Here the calculated atomic multiplet structure of core-level lines $3d$, $4d$, and $5p$ shows very good agreement with the experimental data [1].

This agreement between the calculated atomic multiplet structure and the experimental data in the solid phase does not hold for the corresponding experimental data of free europium atoms with the same half-filled $4f$ subshell.

Godehusen *et al.* [2] have studied the orientation and alignment dichroism [linear magnetic dichroism in the angular distribution (LMDAD)] and linear dichroism in the angular distribution (LDAD) in the $5p$ photoemission of atomic Eu and found marked deviation from the predictions based on a simple LS-multiplet structure of the $5p$-hole states. By coupling the $5p$ hole to the $4f^7(^8S)$ subshell one would expect to see six lines ($^9P_{3,4,5}$ and $^7P_{2,3,4}$ in LS notation). Instead of these six lines a much richer spectrum was observed. Using another coupling scheme, like jK coupling, as proposed by Thole *et al.* [3] for bulk gadolinium, will only shift some lines, but will not change the overall structure.

Figure 1 shows the $5p^{-1}$ photoelectron spectrum of atomic Eu taken at a photon energy of 53 eV. The monochromatized synchrotron radiation of the electron storage ring BESSY I in Berlin was used for the measurements. The spectrum was taken at the U1-TGM5 beamline using a Scienta SES 200 hemispherical electron analyzer. The resolving power achieved with the TGM5 monochromator was $E/\Delta E = 800$ and the electron spectrometer had an experimental bandwidth of 50 meV constant over the whole spectrum. The total instrumental bandwidth amounted to $\Delta E = 80$ meV. The atomic europium beam was produced by a resistively heated Mo crucible.

To shed some light on the complex line structure found in Fig. 1 we have calculated the photoelectron spectra in a configuration-interaction (CI) approximation using the Cowan code [4]. All Slater integrals have been scaled to 80% of the *ab initio* values. For the spin-orbit parameters the unscaled *ab initio* values were used. The Eu ground state $^8S_{7/2}$ is described in a CI approach as a linear combination of $6s^2$, $6s5d$, $5d^2$, and $6p^2$ Hartree-Fock configurations. Using these configurations the ground state can be described by

$$^8S_{7/2} = \sqrt{0.914}|6s^2\,^8S\rangle + \sqrt{0.016}|6s^2\,^6P\rangle - \sqrt{0.010}|5d^2\,^8S\rangle + \sqrt{0.058}|6p^2\,^8S\rangle + \cdots,$$

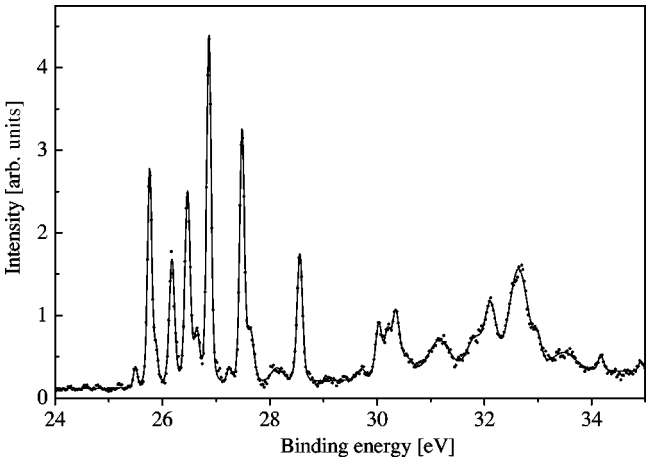

FIG. 1. $5p^{-1}$ photoelectron spectrum of atomic europium taken at $h\nu = 53$ eV.

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TABLE I. Configuration sets used to describe the final ionic states.

Set	Configurations
a	$6s^2$
b	$6s^2,6s5d$
c	$6s^2,5d^2$
d	$6s^2,6s5d,5d^2,6p^2$

which justifies naming the ground state a $6s^2\,{}^8S_{7/2}$, because of the 91.4% contribution of the $|6s^2\,{}^8S\rangle$ basis function. For the $4f^7$ core only ^8S and ^6P parent terms were taken into account. To analyze the atomic Eu photoelectron spectra several different sets of configurations, tabulated in Table I, have been used to model the final state of the photoionization process.

In Fig. 2 the results for these sets are shown. The linewidth was calculated from all possible Auger decays of the $5p$ hole. To take into account experimental broadening all spectra have been convolved with a 80 meV Gaussian.

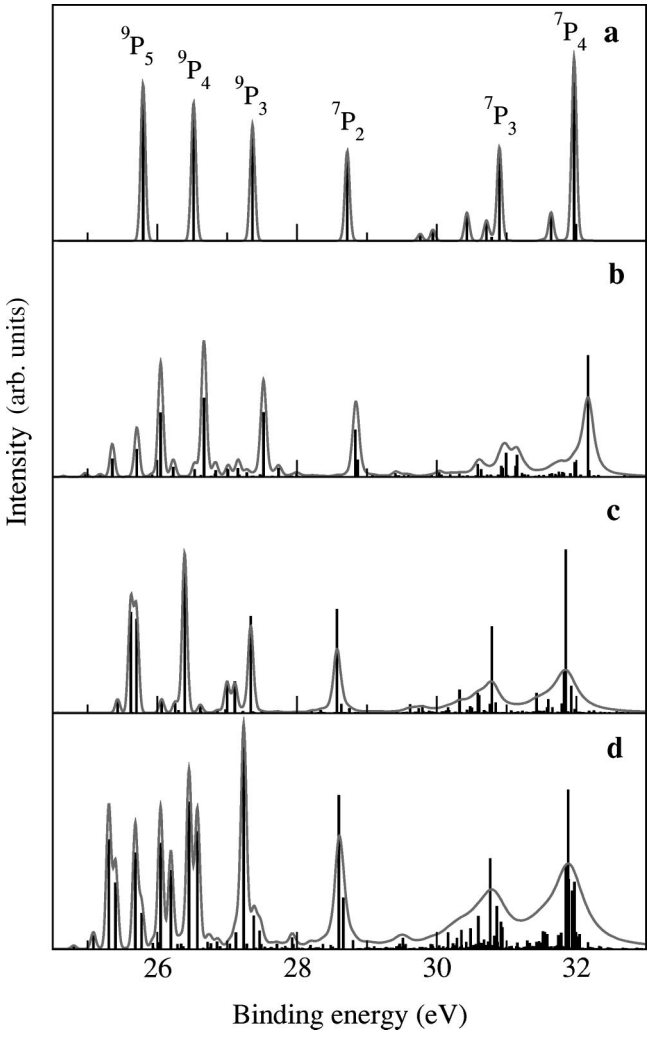

FIG. 2. Calculated photoelectron Eu $5p^{-1}$ spectra using different sets of configurations for the valence shell. The letter in each graph corresponds to the configuration set used in Table I. All spectra have been convolved additionally using an 80 meV Gaussian, to take into account experimental broadening.

In the single configuration approach using the set *a* with the filled subshell $6s^2$ the expected six main lines (in *LS* notation the $^9P_{5,4,3}$ and $^7P_{2,3,4}$ lines) are reproduced [uppermost curve in Fig. 2(a)]. The calculation shows the multiplet splitting in which the $^7P_2$ line is located in the middle between the $^9P_{5,4,3}$ lines and the $^7P_{3,4}$ lines. Therefore the spectrum can be described in neither pure *LS* nor *jj* coupling. This was already found in the analysis of the $5p$ photoemission from Gd films with a similar $5p^{-1}4f^7$ configuration by Thole *et al.* [3].

In addition to these main lines one can discern several satellite lines in the region of the $^7P_{3,4}$ lines, which are due to the recoupling of the $4f^7(^8S)$ subshell to $4f^7(^6P)$ with an energy difference of about 4 eV from the main lines.

The agreement of this calculated spectrum (single configuration approach $6s^2$ and inclusion of the ^6P parent term for the recoupling of the $4f^7$ subshell) with the experimental spectrum in Fig. 1 is by no means satisfactory. The addition of other parent terms ^6L cannot improve the situation as the main discrepancies are in the region of low binding energy between 25 eV and 28 eV. Also, for the lines at higher binding energies the broadening is not reproduced. The addition of other configurations, however, has a tremendous influence on the spectrum, which can be seen in the middle and lower parts of Fig. 2. In Fig. 2(b) the spectrum of a CI calculation including the $6s5d$ configuration is depicted. Including this configuration a line structure in the region of the $6s^2\,{}^9P$ states between 25 eV and 28 eV shows up, which is in much better agreement with the experiment, although there is still a mismatch in the line intensities. However, there is a dramatic change in the linewidth for the higher-binding-energy lines. Including a $5d^2$ configuration instead of the $6s5d$ increases the linewidth of these states even more, which is presented in Fig. 2(c).

Figure 2(d) shows the calculated photoelectron spectrum using set *d*. The final ionic states are now described as a linear combination of the $6s^2$, $6s5d$, $5d^2$, and $6p^2$ configurations. By using this CI expansion a surprisingly good agreement with the experimental data is achieved, which is displayed in Fig. 3. The theoretical spectrum is shifted by 0.4 eV to higher binding energies, to match the energy of line *H* to the $6s^2\,{}^9P_4$ state, and is convoluted in this graph with the experimental resolution.

By including the correlations between $6s$ and $5d$ valence electrons the strong broadening of the high-binding-energy lines can also be described. To get some insight into the broadening effect the lifetimes of the $5p$-hole states have been studied by calculating the Auger decay of the $5p$ hole. In Fig. 4 the linewidth for the $6s^2$, $6s5d$, $5d^2$, and $6p^2$ configurations is shown. As can be seen in the case of the $6s^2$ and also the $6p^2$ configurations the linewidth for all lines is in the range of 1 meV up to 10 meV, resulting in the sharp lines in the calculated photoelectron spectrum of Fig. 2(a). Even the larger number of possible decay channels for the $6p^2$ configuration has only a minor effect on the linewidth, so the larger number of final states is not important.

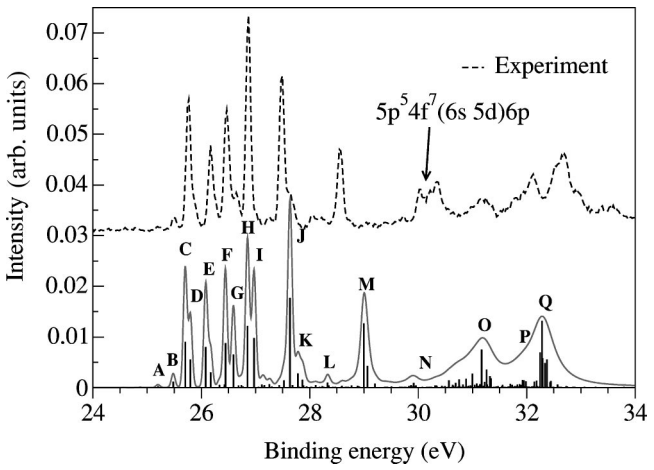

FIG. 3. Comparison of the experimental and theoretical $5p^{-1}$ photoemission spectra of atomic Eu. The experimental spectrum was taken at a photon energy of 53 eV. Here, the theoretical data have been convoluted with the experimental resolution of 80 meV for a better comparison with the experimental data.

However, for a $6s5d$ configuration a linewidth more than one order of magnitude larger is achieved and for the $5d^2$ configuration the linewidth is increased up to three orders of magnitude, which is also to be seen in Fig. 2(b). This dramatic effect can be explained by the possibility of Coster-Kronig and super-Coster-Kronig decay for the states of the $6s5d$ and $5d^2$ configurations, respectively.

Therefore the $6s$-$5d$ correlations have a decisive effect on the line structure in the region of low binding energy (25–28 eV) but they completely determine the line broadening at higher binding energy (28–34 eV).

The explanation for the amazing success of this CI calculation can be found in Table II where the average energies of several configurations Eu^+ $5p^5 4f^7 n\ell n'\ell'$ are listed. The most conspicuous result is a near degeneracy of the $6s$ and $5d$ orbitals caused by the $5p$ hole. There is only a very small energy difference of 10 meV between the configurations

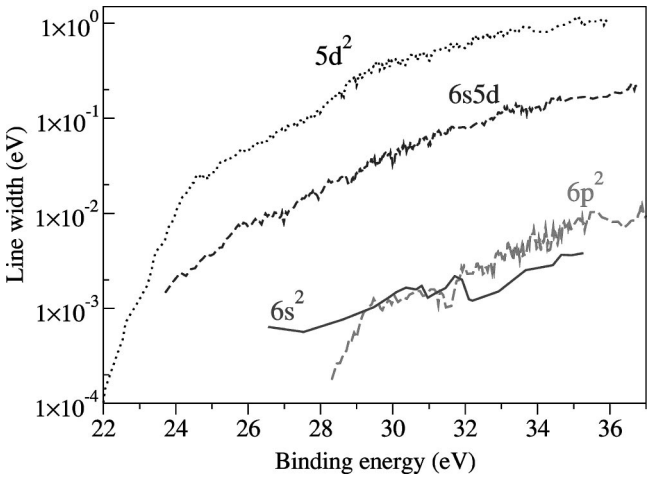

FIG. 4. Average Auger linewidth, corresponding to the Auger lifetime, of all states for the configurations $6s^2$, $6s5d$, $5d^2$, and $6p^2$.

TABLE II. Average energies of the configurations Eu^+ $5p^5 4f^7 n\ell n'\ell'$ relative to the configuration Eu^+ $5p^5 4f^7 6s^2$.

Even parity		Odd parity	
Configuration	E_{av} (eV)	Configuration	E_{av} (eV)
$5p^5 4f^7 6s^2$	0.0	$5p^5 4f^7 6s6p$	2.84
$5p^5 4f^7 6s5d$	0.01	$5p^5 4f^7 5d6p$	3.22
$5p^5 4f^7 5d^2$	1.16	$5p^5 4f^8 6s$	2.21
$5p^5 4f^8 6p$	5.20	$5p^5 4f^8 5d$	3.85
$5p^5 4f^7 6s7s$	6.47		
$5p^5 4f^7 6p^2$	6.95		
$5p^5 4f^7 6s6d$	7.15		
$5p^5 4f^6 6s^2 6p$	8.22		
$5p^5 4f^7 6s6d$	7.15		
$5p^5 4f^7 6s7s$	6.47		

$5p^5 4f^7 6s^2$ and $5p^5 4f^7 6s5d$. Also the configuration $5p^5 4f^7 5d^2$ with an energy difference of 1.16 eV is located nearly at the same energy, resulting in a very strong mixing via final ionic state configuration interaction and a strong excitation of several $6s5d$ and $5d^2$ final ionic states. As shown in Fig. 2, including states of the configuration $5p^5 4f^7 6p^2$ has only a small influence on the line positions, but a strong effect on the intensities of the photolines. Due to the enormous number of states resulting already from the configuration set d we were not able to include further configurations with $4f^6$ or $4f^8$ in the calculation, using the ^8S and ^6P parent terms for the $4f^7$. However, a calculation including only the ^8S parent term could be performed, while the parent terms of $4f^6$ and $4f^8$ were restricted to ^7F. In this approximation there was no effect either on the photoline positions or on the line intensities.

Furthermore, no states of these even parity configurations are located in the energy region below 35 eV, which has been probed with an electronic structure calculation. However, this calculation has shown, that several odd parity states of the configurations $5p^5 4f^7 6s6p$ and $5p^5 4f^7 5d6p$ are located around 30 eV binding energy, where a satellite structure is observed. Therefore we conclude that these satellite lines can be assigned to conjugate shake up processes. From the experimental data an intensity of 15% relative to the main lines can be estimated.

A detailed assignment of the photolines is given in Table III. Here also the amplitudes of the leading eigenvectors are shown.

From these amplitudes one can see immediately that there is a nearly complete mixing of configurations which prevents one from assigning definite configurations to the final ionic states. The near degeneracy of the valence subshells also implies that within a very narrow energy range several states exist with the same total angular momentum J. It is therefore not surprising that in the first analysis of the Eu $5p$ photoelectron spectrum the assignment [2] of the ^9P lines was not correct. Due to the lack of satisfactory calculations we used a more empirical method for the line assignment in the previous paper on the dichroism of free polarized Eu. It was found before [5] that the dichroism of free atoms is a very sensitive

TABLE III. Assignment of the Eu $5p^{-1}$ photolines. For the leading eigenvector the amplitude of the corresponding basis function is given. The accuracy of the experimental energy positions amounts to ±50 meV.

Line	Final ionic state	Leading EV	Energy position (eV) Expt.	Theor.
C	$6s5d\,^9P_5$	25.4%	25.76	25.703
D	$6s5d\,^{11}F_5$	42.9%	25.88	25.799
E	$6s^2\,^9P_5$	21.4%	26.17	26.082
*E*1	$5d^2\,^{11}G_5$	20.4%	26.23	26.172
F	$6s5d\,^9F_5$	24.5%	26.47	25.446
G	$5d^2\,^{11}P_4$	15.4%	26.64	26.592
H	$6s^2\,^9P_4$	28.7%	26.87	26.852
I	$6s5d\,^9P_4$	9.4%		26.972
J	$6s^2\,^9P_3$	37.6%	27.49	27.635
K	$5d^2\,^9P_3$	11.8%	27.66	27.782
M	$6s^2\,^7P_2$	50.8%	28.56	28.997
O	$6s^2\,^7P_3$	13.5%		31.167
Q	$6s^2\,^7P_4$	7.6%		32.283

test for the influence of configuration interaction on the photoionization. With the present results for the multiplet structure we reexamined our previous explanation for the dichroism found in the photoionization of free, laser polarized Eu atoms. Using the calculated line structure we determined the LD and LMDAD spectra of Eu $5p$ (see [6] for details). The LD spectra show remarkable agreement with the experimental spectra, whereas the calculated LMDAD spectrum deviates from the experimental one, mainly in the dichroism for electron lines below 26 eV binding energy. This is a strong hint for additional configuration admixtures that are not yet included in our calculations, which have a strong influence on the dichroism. Since there is a strong photon energy dependence of the LD and LMDAD (e.g., the LMDAD at $h\nu=53$ eV is zero) (see [7]), the line assignment has only a small influence on the results for the phase difference and the amplitudes in this special case. Therefore the values derived in [2] are still valid. The small difference between the measured values for the amplitude ratio x and the phase difference Δ and the results from a single configuration calculation in [2] was already an indication for missing configuration admixtures in the calculation.

From our results we can conclude that the $5p$ photoelectron spectrum of europium is dominated by strong correlation effects between the $6s$, $6p$, and $5d$ valence electrons induced by the $5p$ core hole. The influence of the $6s$-$5d$ correlations has already been shown for Eu $4f$ photoemission [5] where a deviation from the expected $4f^6\,^7F$ multiplet is observed, resulting in a breakdown of the so-called three-parameter model for the photoionization process. For Eu $5p$ photoemission, however, the core-hole-induced degeneracy of the valence subshells gives rise to an even more complex situation where the main multiplet structure of the photoelectron spectrum can be described only by a strong mixture of the configurations $6s^2$, $6s5d$, $5d^2$, and $6p^2$. Furthermore, these correlations induce strong broadening for the higher-binding-energy lines.

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