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LETTER TO THE EDITOR

Angle- and spin-resolved photoelectron spectroscopy of the 4f subshell in atomic ytterbium

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Abstract. The spin polarisation components of photoelectrons from atomic ytterbium have been measured over the photon energy range from 15.5 to 22.5 eV. The measurements were performed by making use of circularly polarised synchrotron radiation from the storage ring BESSY in conjunction with an angle-resolved electron spectrometer. Theoretical predictions based on the relativistic random-phase approximation (RRPA) are in fair agreement with the experimental data even though a certain offset between theory and experiment exists.

The photoelectron spin polarisation effects with unpolarised atoms are exclusively due to the existence of the spin–orbit interaction. The magnitude of the spin polarisation has however been shown to be almost independent of the strength of the spin–orbit coupling. Thus the dynamical spin parameter ξ and its kinetic energy dependence has, in an angle-, energy- and spin-resolved photoemission experiment, been found to be very similar for the respective 3p, 4p and 5p levels in Ar, Kr and Xe (Heinzmann *et al* 1979, 1980, Heinzmann 1980), which in first order verifies the importance of *LS* coupling. Deviations from the *LS* approximation are due to the growing influence of spin–orbit interactions on the continuum wavefunctions with increasing atomic weight. With the spin- and angle-resolved experimental set-up at BESSY it has recently become possible to characterise all the dynamical spin parameters A, α and ξ needed in order to describe the electron spin polarisation vector, where A is the angle-integrated spin polarisation transfer from circularly polarised photons onto the photoelectrons, α is the asymmetry parameter of the angle-dependent spin polarisation transfer $A(\theta)$ and ξ is the spin parameter describing the spin polarisation component $P_\perp(\theta)$ perpendicular to the photoionisation reaction plane using any degree of polarised light. The three spin polarisation parameters form together with the total photoionisation cross section, σ, and angular distribution parameter, β, a set of data needed in order to completely describe quantum mechanically the photoionisation process. Until now a complete characterisation of photoionisation has only been carried out for electrons originating from s, p and d shells in Xe (Heckenkamp *et al* 1986b) and Hg (Heinzmann 1987, Schäfers *et al* 1988). However, for an f shell, where only σ and β have been known (Svensson *et al* 1986), it has not been possible to form a similar dataset since no information has been gained so far about the properties of the spin polarisation vector.

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In this letter we discuss the measured and calculated energy dependence of the dynamical spin parameters of the 4f electrons in free ytterbium in order to record how an increase in the angular momentum will affect the electron spin polarisation vector. Yb is a favourable test case for this purpose since it is a closed-shell atom, which simplifies both experimental and theoretical treatment and interpretation. Also presented are some experimental results for the spin polarisation of the 6s electrons in Yb.

The experimental set-up for the spin polarisation measurements has been described earlier in detail by Heckenkamp (1986a) and Heinzmann (1987). We show a schematic diagram of the apparatus in figure 1. Briefly, a 6.5 m normal incidence monochromator with a spherical mirror and plane grating (1200 lines/mm) uses the electron beam in the storage ring BESSY as a virtual entrance slit. Apertures movable in the vertical direction are used to select radiation emitted above and below the plane of the storage ring which has positive or negative helicity, respectively. In the experiment a bandpass of 1 nm was used which in the interaction region gave a measured photon flux of some 10^{11} photons/s. Polarisation of the light was measured with a four-mirror analyser. The circularly polarised and monochromatised synchrotron radiation is crossed with the atomic beam in an electric- and magnetic-field-free region. A simulated hemispherical electron analyser (Jost 1979), rotatable in the interaction plane, is utilised to energy analyse the photoelectrons. After two 90° deflections the electrons are accelerated to 100 keV and scattered by the gold foil of a Mott detector. The cross section of Yb is low in the investigated energy region and typical count rates in the Mott detector were of the order of 0.2–0.5 counts/s. As can be seen in figure 1, the transverse components $A(\theta)$ and $P_\perp(\theta)$ are simultaneously determined by two pairs of detectors.

The experimental results together with the theoretical calculations for the dynamical spin parameters A, α and ξ for the spin-orbit components $4f_{7/2}$ and $4f_{5/2}$ are presented in figure 2. In the photon energy region chosen for these measurements, 15.5–22.5 eV, the continuum is unperturbed by resonances. Due to the low intensity of the photoelec-

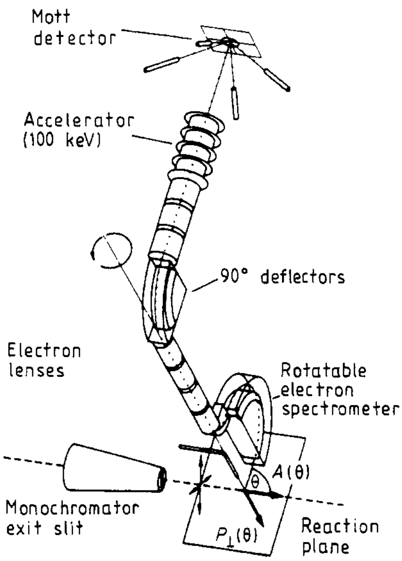

Figure 1. Schematic diagram of the experimental set-up in use at BESSY.

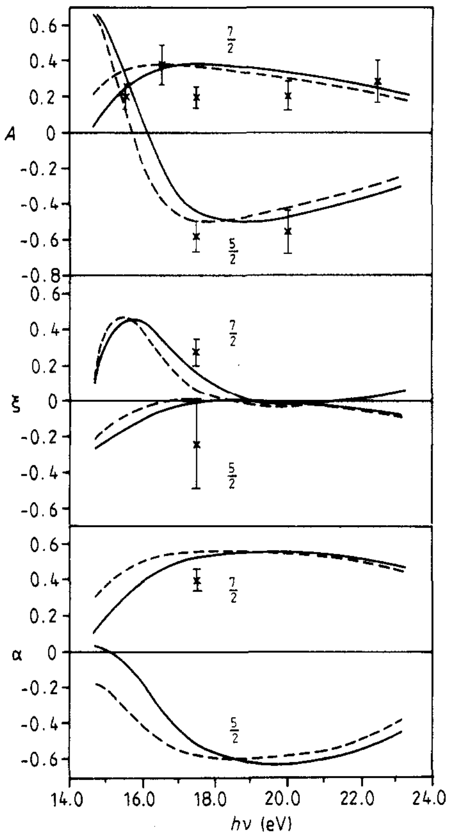

Figure 2. Experimental results of the spin polarisation parameters A, α and ξ for the spin-orbit doublet 4f in atomic Yb. The data are compared with theoretical RRPA calculations: velocity form, full curve; length form, broken curve.

tron current it was only possible to study the angular distribution $A(\theta)$, and thus α for the $4f_{7/2}$ electron, at one photon energy, $h\nu = 17.5$ eV. At this energy, however, we could determine all three spin parameters for the $4f_{7/2}$ electron and the two parameters, $A_{5/2}$ and $\xi_{5/2}$, for the $4f_{5/2}$ electron. Together with an earlier experimental and theoretical investigation of the angular distribution parameters β and partial cross sections σ (Svensson *et al* 1986), our present results at $h\nu = 17.5$ eV represent a parameter set which for the first time offers information needed in order to completely describe quantum mechanically the photoionisation process in an f subshell.

The theoretical calculations were performed in the framework of the relativistic random-phase approximation (RRPA) (Johnson and Lin 1978, Johnson *et al* 1983). All 13 channels obtained by *jj*-coupled dipole excitations of the 6s, 4f and 5p subshells have been included in the calculations:

$$6s_{1/2} \rightarrow \varepsilon p_{1/2}, p_{3/2}$$
$$4f_{7/2} \rightarrow \varepsilon d_{5/2}, g_{7/2}, g_{9/2}$$
$$4f_{5/2} \rightarrow \varepsilon d_{3/2}, d_{5/2}, g_{7/2}$$
$$5p_{3/2} \rightarrow \varepsilon d_{3/2}, d_{5/2}, s_{1/2}$$
$$5p_{1/2} \rightarrow \varepsilon d_{3/2}, s_{1/2}.$$

It was necessary to take into account correlation with the 5p sublevel in order to predict the spin parameters theoretically. To achieve fair agreement between theory and experiment for β and σ the inclusion of the correlation with the 5p subshell was however of small importance and was omitted in the previous study by Svensson *et al* (1986).

The theoretical curves for the spin transfer $A_{7/2}$ and $A_{5/2}$, although within the experimental error limits, seem systematically shifted towards higher polarisation values with respect to the experimental results. The experimentally measured angular distribution of $A(\theta)$ for the $4f_{7/2}$ electrons at $h\nu = 17.5$ eV is shown in figure 3 together with a least-squares fit. The fit gives the values $A_{7/2} = 0.27 \pm 0.05$, $\alpha_{7/2} = 0.41 \pm 0.07$ and $\beta_{7/2} = 0.72 \pm 0.30$ (Caffola 1987). Judging from only one experimental point for $\alpha_{7/2}$ at $h\nu = 17.5$ eV, the theoretical curve for the same parameter seems overestimated and falls just above the limit of experimental uncertainty. Worth noticing is that our theoretically predicted value for $\beta_{7/2}$ agrees within the experimental error bars at the same photon energy (Svensson *et al* 1986). At the present stage we can conclude that theory and experiment overlap for the ξ parameters.

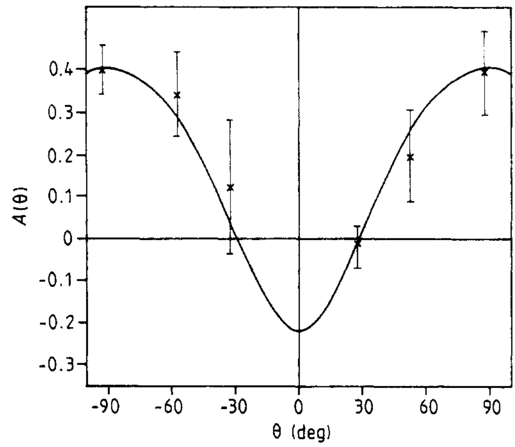

Figure 3. Angular dependence of the spin polarisation component $A_{7/2}$ (θ). Included in the figure is a least-squares fit (full curve) which gives the dynamical parameters $A_{7/2} = 0.27 \pm 0.05$, $\alpha_{7/2} = 0.41 \pm 0.07$ and $\beta_{7/2} = 0.72 \pm 0.30$.

In *LS* coupling the influence of the spin-orbit interaction in the continuum is neglected. The ratio of the spin transfer, $A_{l+1/2}/A_{l-1/2}$, has for this case been shown (Cherepkov 1983) to be inversely proportional to the negative statistical ratio. When the photoelectrons correspond to the two components in a spin-orbit doublet the relation for the A parameter given above no longer applies, but if used the deviations from the inversely statistical ratios are usually found to be small. Where a fine-level splitting exists, the following limits for the spin transfer are valid when spin-orbit interaction in the ground state is accounted for (classical limits):

$$-\tfrac{1}{2} \leq A_j \leq (l+1)/2l \qquad \text{for } j = l - \tfrac{1}{2}$$

and

$$-\tfrac{1}{2} \leq A_j \leq l/2(l+1) \qquad \text{for } j = l + \tfrac{1}{2}$$

and $|A_j| \leq 1$ when spin-orbit interactions in both the ground and continuum states are included (relativistic limits) (Cherepkov 1983).

Figure 4 shows the experimental and theoretical curves for the spin transfer in the 5p subshell of Xe (Heckenkamp *et al* 1984) and in the 5d subshell of Hg (Schäfers *et al* 1988) as a reference. In both Xe and Hg the ratios formed from the experimentally measured A parameters are indeed very close to the statistical ratios with opposite signs. It can also be seen that the experimental values A_j for the spin-orbit components of Xe as well as Hg are within the classical limits. Even so, it has been shown that relativistic effects are important in both Xe and Hg.

Forming the ratio $A_{7/2}/A_{5/2}$ from the experimental values for Yb, we find over the investigated photon energy region the ratio -0.47 ± 0.15, which significantly deviates from the statistical ratio of -0.75. We also find that experiment gives values for $A_{5/2} = -0.57 \pm 0.12$, which might be less than -0.5, the classical limit for this component. It is now interesting to note two things: firstly, the properties of the spin parameter A for the f electrons in Yb cannot even in the first approximation be predicted classically—which was the case for p electrons in Xe and d electrons in Hg—and secondly, the spin-orbit splitting is equal to 1.3 eV in both the $4f^{14}$ level of Yb and the $5p^6$ level of Xe.

In terms of dipole matrix elements and phaseshift differences, the A parameters for the 4f spin-orbit doublet in Yb are given as (Cherepkov 1983)

$$A_{5/2} = \frac{0.28(d_{d^{3/2}})^2 + 0.01(d_{d^{5/2}})^2 - 0.50(d_{g^{7/2}})^2 + 0.37 d_{d^{3/2}} d_{d^{5/2}} \cos \Delta_1}{0.93(d_{d^{3/2}})^2 + 0.07(d_{d^{5/2}})^2 + (d_{g^{7/2}})^2}$$

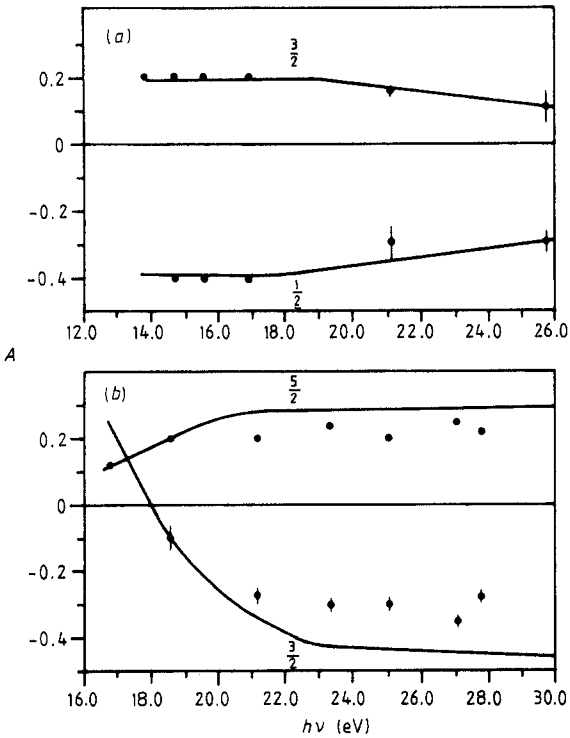

Figure 4. The dynamical spin parameters A for (a) the spin-orbit doublet 5p in Xe (Heckenkamp *et al* 1986) and (b) 5d in Hg (Schäfers *et al* 1987). Experimental results are represented with full or open circles and are compared with RRPA calculations (for Xe: Huang *et al* (1981) and for Hg: Johnson *et al* (1982)), which are indicated by full curves.

and

$$A_{7/2}=\frac{-0.500(d_{d^{5/2}})^2-0.003(d_{g^{7/2}})^2+0.594(d_{g^{9/2}})^2-0.217(d_{g^{7/2}})(d_{g^{9/2}})\cos\Delta_2}{(d_{d^{5/2}})^2+0.028(d_{g^{7/2}})^2+0.972(d_{g^{9/2}})^2}.$$

From an analysis of the formulae given above it is easy to find that the non-relativistic approximation would give a ratio of $A_{7/2}/A_{5/2}$ that agrees with the statistical ratio but not with experiment. Similarly, it is possible to find that no single matrix element can be neglected—despite the fact that the factors in front of them at times indicate that their weight is very small—in order to reproduce the experimentally found value for this ratio. We conclude therefore that the 4f electrons in Yb have to be treated relativistically, i.e. spin-orbit interaction must be included in the ground and final states. The reason for the relativistic nature of the 4f subshell in Yb near threshold is very likely to be due to a high potential barrier created by the g continuum wave forcing the f electrons to couple to the d continuum as the major exit route left open. It was shown in the earlier study on Yb (Svensson *et al* 1986) and also pointed out by Keller (1987) that the 4f partial cross section in Yb does not reach its maximum until $h\nu$ is about 90 eV. This delayed onset for the f partial cross section shows that the $4f\rightarrow\varepsilon g$ channel is indeed very weak in our energy region.

When electrons from the 6s subshell are photoionised, Yb^+ is left in an ionic state that has no fine-structure splitting. Still, we have measured the spin polarisation parameter $A_{1/2}$ for the 6s electrons and found it to be -0.37 ± 0.16 at $h\nu=17.5$ eV and -0.33 ± 0.50 at $h\nu=20.0$ eV. This is yet one more indication of the relativistic nature of the photoionisation process in Yb since a non-vanishing spin polarisation of the photoelectrons shows directly the influence of spin-orbit interaction in the continuum states, in this case between $\varepsilon p_{1/2}$ and $\varepsilon p_{3/2}$.

The measurements we have described in this letter represent a first step towards a complete analysis and understanding of the photoionisation process in an f subshell. Due to the weakness of the $4f\rightarrow\varepsilon g$ channel in Yb the inclusion of relativistic effects is of great importance in order to be able to analyse the experimental and theoretical results. As is known from other studies, RRPA does not account satisfactorily for all important correlations near threshold (e.g., the relaxation effects are not accounted for), which could explain the apparent shift between the experimental data and the theoretical results in this study.

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