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Photoeffect in the 4d subshell of atomic silver between 14 and 140 eV†

M O Krause‡, W A Svensson‡||, T A Carlson‡, G Leroi§¶, D E Ederer§, D M P Holland§* and A C Parr§

‡ Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA
§ National Bureau of Standards, Gaithersburg, Maryland 20899, USA

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Abstract. Relative partial photoionisation cross sections and the photoelectron angular distribution parameter β have been measured for the 4d electrons of atomic silver in the energy range $14 \leqslant h\nu \leqslant 140$ eV. Data are found to be in good agreement with the results calculated in the relativistic random-phase approximation (RRPA) for the neighbouring atom palladium. Comparison with solid-state data reveals a dominant atomic character of the 4d electrons in metals. This is especially evident for the β parameter. However, differences occurring around the Cooper minimum at 130 eV show the influence of the metallic state on the properties of the 4d electrons.

1. Introduction

Silver is a suitable candidate for a photoionisation study of 4d electrons that are sufficiently weakly bound to dominate the electronic dynamics at low photon energies. The experimental data obtained from free silver atoms can be compared (i) with theoretical predictions that have been made for the neighbouring, closed-shell element Pd and (ii) with results obtained from silver in the metallic state. Specifically, we compare the partial photoionisation cross sections, σ(4d), and photoelectron angular distribution parameters, β(4d), with the relativistic random phase approximation (RRPA) calculation for palladium by Radojević and Johnson (1983) in the photon energy range from 14 to 140 eV. In this range, the presence of a delayed maximum induced by the centrifugal barrier acting on the 4d electrons and the occurrence of a Cooper minimum (near 135 eV) place strict demands on the accuracy of the theoretical model. The atomic values of σ and β that are contrasted with the corresponding values in the metal allow us to examine to what extent the 4d electrons retain their atomic character in the metal, in which they have become part of the conduction band.

We previously reported results of an initial experiment on Ag (Krause *et al* 1981b), and some of our β data appeared in the theoretical paper by Radojević and Johnson (1983). In the present paper we summarise and discuss the final results on both the cross sections and the angular distribution parameters.

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|| Present address: Royal Institute of Technology, S-10044, Stockholm, Sweden.
¶ Permanent address: Chemistry Department, Michigan State University, East Lansing, Michigan, USA.
* Permanent address: Daresbury Laboratory, Warrington WA4 4AD, England.

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2. Experimental

The experimental approach and conditions were similar to those described previously (Krause *et al* 1981a, 1984). Briefly, the photoelectrons ejected from Ag atoms by synchrotron radiation were detected, following energy analysis, at 0, 90° and the magic angle measured relative to the major polarisation vector of the photon beam; the cross section σ(4d) and angular distribution parameter β(4d) were derived from the resulting photoelectron signal (Krause *et al* 1984). Many of the spectra were obtained using two electrostatic energy analysers located at right angles to each other in a plane perpendicular to the photon beam. However, in the latter stages of the work, a third analyser was placed on the same platform, opposite one of the existing analysers, to allow the continuous and simultaneous recording of a reference spectrum for the cross section determination at the magic angle setting.

The two photon sources used in this study were the Synchrotron Radiation Center, SRC, Wisconsin and the SURF-II Storage Ring at the National Bureau of Standards, NBS, Maryland. Monoenergetic photons having a bandpass of approximately 20 nm were obtained by employing four monochromators with overlapping energy ranges: a TGM (toroidal grating) from 20 to 115 eV, an ERG (extended-range grasshopper) from 40 to 140 eV, a Seya from 14 to 35 eV and a 2 m NIM (normal incidence) from 14 to 25 eV. In regions where different monochromators overlapped we found very good agreement between the data sets for β and satisfactory accord for the σ data. For example, the NIM β values obtained at the NBS agree with the Seya values obtained at the SRC within 0.05 units.

Silver was evaporated from a Ta oven heated resistively to about 1250 K at an ambient pressure of $(4\text{–}15)\times10^{-6}$ Pa (in the early stages of the work it was 10^{-4} Pa or less). The vapour density in the source cell was estimated to correspond to $(2\text{–}5)\times10^{-2}$ Pa.

The power to the oven was supplied by a constant-current source. As a result the operation of the vapour source was extremely stable. However, the gradual closing-up of the entrance hole to the electron source cell by the metal deposit caused a slow decrease in the signal during the first hours of operation, and a faster decrease toward the end of an operational day. A selected reference spectrum was recorded periodically to correct for this effect, which would otherwise have been deleterious to the σ determinations. The effect did not influence the β determinations that were obtained from the signals of two analysers operated simultaneously. Each point required an acquisition time of typically 15–20 min except at the higher energies where 30–40 min were needed.

At a bandpass of typically 20 nm and an energy resolution $\Delta E/E = 0.01$ of the analysers the 4d multiplet could not be resolved in the photoelectron spectra except at the low photon energies, $h\nu \leqslant 25$ eV. Hence, all data presented here were averaged over the 4d multiplet structure. Typically four separate data points were measured for each of the selected photon energies.

3. Results and discussion

The angular distribution parameter values are displayed in figure 1 and the partial cross section data are shown in figure 2. A tabulation of the data is given in tables 1 and 2. Our data on atomic Ag are averaged results from various runs made at different monochromators over a period of time. The error bars reflect uncertainties in the

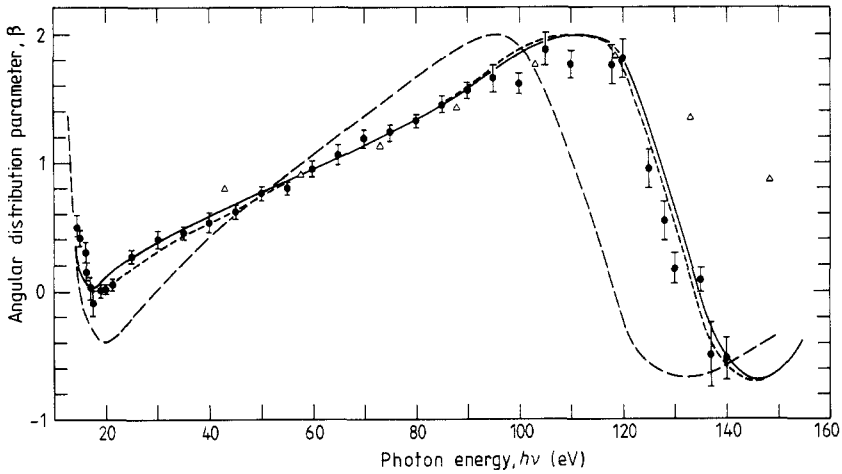

Figure 1. Comparison of the present β values (●) for the 4d electrons of atomic Ag with the RRPA results of Radojević and Johnson (1983) (——, velocity form; - - - -, length form) and the HS calculations of Manson (1983) (- - -) as well as the data for Ag metal by Davis *et al* (1980) (△). The RRPA curves given in the length and velocity forms are shifted by +3.2 eV to account for the difference in ionisation potential between Pd and Ag. Our data are averaged over the components of the 4d quartet.

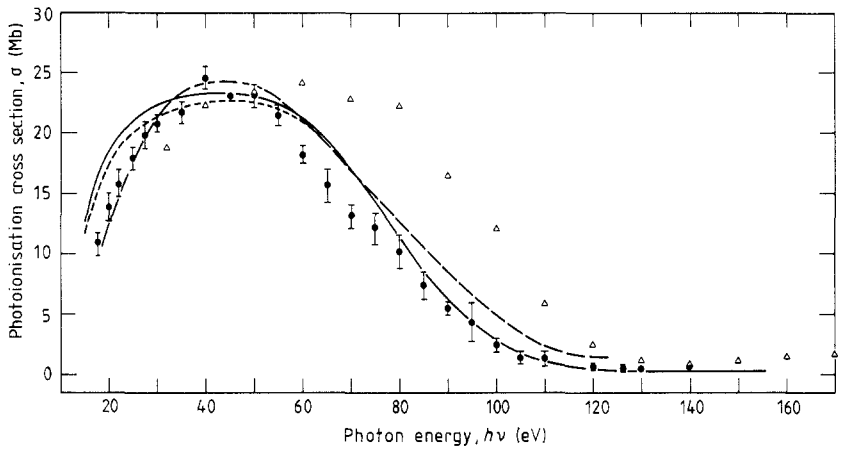

Figure 2. The partial photoionisation cross section for 4d electrons of Ag. Our atomic values (●) are compared with the RRPA prediction for Pd by Radojević and Johnson (1983) (——, velocity form; - - - -, length form), the HS results by Combet-Farnoux (1972) (- - -) and the measurements for metallic Ag by Wehner *et al* (1976) (△). Note that the experimental data are normalised at 45 eV to the RRPA theoretical value that is averaged between the length and velocity results.

calibration, the statistical error and the scatter between the various runs. The β(4d) values differ slightly from our data presented by Radojević and Johnson (1983), because more data were added since the publication of their paper. The β values obtained in the initial experiment (Krause *et al* 1981b) were found to be somewhat too high due to the then insufficiently known shape of the electron source. Also plotted in figures 1 and 2 are the theoretical calculations in the Herman-Skillman (HS) model for β (Manson 1983) and σ (Combet-Farnoux 1972) and the predictions in the relativistic

Table 1. The angular distribution parameter β for 4d electrons of atomic silver.

$h\nu$ (eV)	β	$h\nu$ (eV)	β
14.5	0.5 (1)	65	1.06 (8)
15.0	0.41 (5)	70	1.18 (7)
15.5	0.30 (8)	75	1.23 (6)
16.0	0.0 (1)	80	1.32 (5)
16.5	0.15 (6)	85	1.45 (7)
16.8	0.0 (1)	90	1.56 (6)
17.2	0.01 (6)	95	1.65 (11)
17.5	−0.10 (5)	100	1.61 (8)
18.0	−0.03 (5)	105	1.88 (13)
19.1	0.00 (5)	110	1.76 (10)
20.0	0.01 (3)	118	1.76 (15)
21.2	0.05 (4)	120	1.80 (15)
25.0	0.27 (5)	125	0.95 (15)
30	0.41 (6)	128	0.54 (15)
35	0.45 (5)	130	0.17 (12)
40	0.53 (8)	135	0.08 (10)
50	0.76 (5)	137	−0.50 (25)
55	0.80 (5)	140	−0.53 (16)
60	0.95 (6)		

Table 2. Relative photoionisation cross sections for 4d electrons of atomic Ag. Data are normalised to 100 at $h\nu = 45$ eV[a].

$h\nu$ (eV)	σ_{rel}[b]	$h\nu$ (eV)	σ_{rel}[b]
18	47 (4)	70	57 (4)
20	60 (5)	75	53 (6)
22	69 (5)	80	44 (6)
25	78 (4)	85	32 (5)
27.5	86 (5)	90	24 (2)
30	90 (3)	95	19 (7)
35	94 (4)	100	11 (2)
40	107 (4)	105	6 (2)
45	100	110	6 (2)
50	100 (4)	120	3 (1)
55	93 (4)	125	2 (1)
60	79 (3)	130	2 (1)
65	68 (6)	140	4 (1.5)

[a] For use in figure 2, these experimental data were normalised to the theoretical value of 24 Mb at $h\nu = 45$ eV.

[b] The quoted errors do not include the uncertainties (3–4%) in the cross sections of the rare gases used for calibration of the grating efficiency by the PAX method.

random-phase approximation (RRPA) for both β and σ (Radojević and Johnson 1983). Data pertaining to Ag metal were reported previously; we plot in figure 1 the β values obtained by Davis *et al* (1980) and in figure 2 the σ values reported by Wehner *et al* (1976). It should be noted that all experimental σ values are normalised to the RRPA results at $h\nu = 45$ eV.

Considering the atomic aspects of the results first, we find a good accord between our data and the RRPA results for Pd (Radojević and Johnson 1983). Ideally, the

theoretical predictions should pertain to Ag, but the calculation for the open-shell atom Ag is more difficult (although the 5s subshell is *half* filled) than for the closed-shell atom Pd which precedes Ag in the periodic table. Fortunately, the properties of the 4d electrons do not change abruptly in this Z region, so that a comparison between adjacent elements is not expected to introduce an unacceptable uncertainty. We did, however, make an allowance for the known differences by shifting the 4d ionisation potential from Pd to Ag, $\Delta E \simeq 3.2$ eV. This shift improves the agreement at the low photon energies. At energies above 60 eV, a still better agreement than seen in the figures could be achieved if we were to correct the theoretical curve by a factor $Z^2(\mathrm{Pd})/Z^2(\mathrm{Ag})$ to account approximately for the change in the nuclear field.

The agreement between the HS results (Manson 1983, Combet-Farnoux 1972) and the experimental data is surprisingly good. This shows, as indicated earlier (Krause 1980), that correlation effects are weak. However, the comparison of the RRPA prediction with the experiment shows that these weak effects, such as the 4d intrashell correlations, must be considered in order to achieve a quantitative agreement with the experimental results.

Several detailed features of the results should be noted. The position of the Cooper minimum can be easily determined from the β curve in the case of the experiment. In the dipole approximation, the minimum occurs at $\beta = 0.2$ for d electrons and hence at a photon energy of 131 ± 2 eV. This value is in very good agreement with the RRPA value, which is 136 eV for Pd. By contrast, the calculations by Manson (1983) and Combet-Farnoux (1972) using the HS model placed the minimum at 117 and 123 eV respectively. Most of the energy range covered in this experiment is free of resonances, hence excitation of electronic configurations other than the 4d subshell will have no pronounced influence on the 4d ionisation process. A possible exception occurs near 100 eV, where the excitation of a 4p electron could be responsible for the slightly lower β value seen in figure 1.

Below 19 eV a number of autoionisation resonances involving two-electron excitations are possible (Connerade and Baig 1979). We have, in fact, observed excursions in the β parameter up to 0.5 units near such resonances, as well as different partial β and σ values for the individual multiplet components. However, this region was not investigated in detail and the points shown in figure 1 below 19 eV are values averaged over suitable energy intervals, where no resonance states were suspected.

As noted above, the σ data are matched at 45 eV with the RRPA datum in the absence of an absolute cross section determination for the metal vapour. As a consequence the comparison between our data and theory, and other data, pertains only to the *shape* of the curves. An estimate of the absolute partial cross section $\sigma(4\mathrm{d})$ can be made by equating $\sigma(4\mathrm{d})$ with the total cross section determination $\sigma(\mathrm{tot})$ for the metal. The value of σ (tot) is about 20 Mb at 35 eV as reported by Haensel *et al* (1967). This cross section which would include a 1% contribution from 5s ionisation (Krause 1980) and perhaps 10% for the two-electron processes is somewhat lower than the RRPA value of 22.5 Mb. The 10–20% discrepancy might be resolved by a direct vapour phase determination of the photoionisation cross section.

Above 18 eV, the $\sigma(4\mathrm{d})$ curve rises somewhat more steeply than the RRPA results and slightly more rapidly than the earlier data (Krause 1980) obtained with the use of discrete discharge sources.

A second aspect of this study concerns the relation of the atomic data to the solid-state data. In figure 1 the β values for Ag metal (Davis *et al* 1980) are shown alongside our atomic data, and in figure 2 the σ values for Ag metal measured by

Wehner *et al* (1976) are shown. The latter values are tied to the atomic results at $h\nu = 45$ eV. For the β parameter we find a striking agreement between the atomic and metallic values between 40 and 120 eV, which includes the region of the delayed 4d maximum. However, the dip of β near the Cooper minimum is seen to be much shallower in the metal than in the atom. By contrast, the σ data for Ag metal, while showing the same general trend as the atomic data, appear to be displaced toward higher energies; the maximum occurs near 60 eV instead of 45 eV as for the atom, the rise toward the maximum being more delayed and the position of the Cooper minimum at about 140 eV instead of 131 eV as for the atom. In the work of Rossi *et al* (1983), the σ curve for the metal is shifted to even higher energies whereas σ(4d) obtained from an overlayer of Ag on Si III shows the same trend as the results of Wehner *et al* (1976) for the metal. The reason for the discrepancy between the two sets of data for the metal is not entirely clear. We note, however, the difficulties associated with quantitative σ determinations from solid-state photoelectron spectra. An important source of error, elastic scattering, has been discussed recently by Baschenko *et al* (1984). These same errors that enter the σ measurements are effectively eliminated in the β(4d) determinations in amorphous metal, because the β parameter is obtained from the *ratio* of *two* photoelectron intensity measurements. Therefore, the comparison between the atomic and metallic data should rely mainly on the determination of the β parameter.

The similarity of the β values for the metal and the atom indicates that the 4d electrons retain their atomic character in the metal, although they have become part of the conduction band. The atomic character can be understood on the basis that the 4d electron band, about 3.1 eV wide, lies approximately 3.2 eV below the Fermi edge (Moruzzi *et al* 1978) which gives them a largely localised, and hence atomic, behaviour. However, the condensed matter effects, though evidently small in Ag, can be seen in the region of the Cooper minimum, which is especially sensitive to the details of the wavefunctions, electron–electron interactions and the possibility of additional open channels. We observe a decreased depth of the Cooper minimum in the metal and this effect might be attributed to two factors: a modification of the 4d wavefunctions in the condensed phase and the presence of electrons of other symmetries in the region of the conduction band that was selected for the measurement because of its high density of d electrons. To what extent each of the factors contributes cannot be evaluated from the β measurements alone.

The pronounced dependence of the β parameter near the Cooper minimum on the state of bonding shown here for silver in the atomic and metallic states has previously been observed for electrons in simple molecules. For example, the lone-pair orbital, 1π, in the hydrogen halides displays a deep minimum, while the bonding orbital, 3σ, exhibits a shallower minimum (Carlson *et al* 1984). In that case, the minimum for 1π resembles that for the p electrons of the rare gases, because the lone-pair orbital which is made up of the halide p electrons is essentially atomic. By contrast, the minimum for 3σ is shallow, because this bonding orbital provides a greater number of ionisation channels, some with and some without a Cooper minimum.

4. Conclusions

A measurement of the dynamic parameters, σ and β, for the 4d electrons in atomic Ag has provided data from threshold through the delayed maximum to the Cooper

minimum. A comparison with the RRPA results which were carried out for the closed-shell atom Pd shows excellent agreement between experiment and theory. This is significant because the results respond sensitively to the details of the centrifugal barrier that causes the delayed maximum and the position of the radial node in the ground-state 4d wavefunctions that causes the Cooper minimum. The results can also be considered representative of the weakly bound 4d electrons in nearby elements whose low-energy properties are closely associated with the 4d subshell. Although sophisticated theory, such as the random-phase approximation, is needed to achieve a quantitative description of the dynamic parameters, we find the simple Herman–Skillman calculations useful to yield a semi-quantitative overall view of the behaviour of the 4d electrons.

Although Ag is an open-shell atom, we did not examine this aspect in detail. We point out, however, that the components of the 4d quartet were seen to exhibit individual behaviour just above threshold and in the region of autoionisation below 19 eV.

A comparison of condensed matter data with the atomic data shows that the 4d electrons retain their atomic character to a great extent in the metallic state. Deviations occurring for the β parameter in the Cooper minimum are indicative of the 'solid-state effects' and attest to the value of measurements in the minimum region to detect the modifications of the electronic properties that are introduced by the condensed and the chemical state.

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