Spin-Resolved Auger Electron Spectroscopy of Barium Atoms

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The angular dependence of the spin polarization of Auger electrons was measured after $5p$ photoionization of free Ba atoms with circularly polarized light. A substantial polarization transfer from the oriented photoion onto the Auger electrons was observed in confirmation of theoretical predictions by Kabachnik and Lee. The ratio of the dipole transition matrix elements and the orientation and alignment coefficients were extracted from the experimental data for the Auger electron polarization parameters.

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In ionization, creation of vacancies in inner atomic shells by photon or particle impact often gives rise to subsequent Auger decay. In their emission characteristics these Auger electrons reflect a possible nonstatistical population of the magnetic substates of the intermediate ionic state produced by the initial impact [1]. Consequently, as discussed in the general reviews of ion alignment by Mehlhorn [2], angle-resolved electron spectroscopy is a technique to analyze the alignment and its influences on the Auger electron angular distribution. Using synchrotron radiation, this was studied more recently by several groups (see, e.g., Refs. [3-5]). The anisotropy of the photoprocess is moreover strongly reflected in the spin polarization of the ejected electrons. There are essentially two ways to obtain spin-polarized Auger electrons from unpolarized atoms. Either a polarization of the incident projectile may induce a hole orientation or an anisotropic interaction may cause an alignment of the intermediate ionic state leading both to the emission of spin-polarized Auger electrons. This was first pointed out by Klar [6], who called the first process *polarization transfer* and the second *dynamical polarization.* The first case connected with an orientation of the vacancy state was later discussed in detail theoretically by Kabachnik and Lee [7]. For ionization with circularly polarized light, all three components of the spin-polarization vector can be nonzero and, in general, the component in the light direction, $A(\theta)$, can have a pronounced dependence on the angle θ between the photon and electron momentum. In contrast, as required by symmetry, for a purely dynamical polarization there exists only a polarization component $P_\perp(\theta)$ normal to the reaction plane. The alignment is generally small, except in the region of a Cooper minimum or near threshold, where the partial wave with larger angular momentum may be suppressed by a centrifugal barrier [8]. A small alignment in turn results in a small polarization component $P_\perp(\theta)$ and in a weak angular dependence of the Auger electron intensity.

All previous studies of Auger electrons emitted from free atoms were carried out using particle impact or linearly polarized light for ionization causing only an alignment of the photoion. Only one group reported measurements of the dynamical polarization after alignment by electron or proton impact ionization [9,10]. However, the Auger electron spin polarization was very small (ca. 1%). For photon impact, polarized Auger electrons have otherwise only been examined in photoemission from solid surfaces [11,12]. Here, the local environment of the hole state as well as the surface magnetization or the screening by conduction band electrons influence the resulting polarization strongly. For free magnesium atoms a complete experiment in the *LS* coupling scheme was carried out in a spin-unresolved investigation of the cross section and the angular distribution of the photo- and Auger-electron emission [13]. But in more complex cases and as a check of the validity of the theoretical assumptions more independent information can be obtained by electron spin polarization analysis. In particular, ionization with circularly polarized light creating an intermediate photoion state which is not only aligned but also oriented should yield further information about the underlying two-step double-ionization process (see also Ref. [14]). In the case of a ${}^1S_0$ final ionic state, discussed here, it is possible to determine directly the orientation of the intermediate state from the spin-polarization parameters. Here, we present the first measurements of the spin polarization of Auger electrons emitted after photoionization of free atoms with circularly polarized light.

The angle- and energy-resolved measurements of the spin-polarization components $A(\theta)$ and $P_\perp(\theta)$ and of the electron intensity were performed with circularly polarized light from the 6.5 m normal-incidence monochromator [15] (resolution: 0.18 nm FWHM) at the Berlin electron storage ring BESSY. The apparatus contains a rotatable simulated hemispherical electron spectrometer operated in conjunction with a Mott detector as described elsewhere [16]. For circularly polarized light, all dynamical information in addition to the cross section can be extracted from the angular distributions of two spin-polarization components which can be expressed in terms of the dynamical parameters A, ξ, α, and β, the second Legendre polynomial $P_2(\cos\theta)$ and the light helicity γ [16]:

$$A(\theta)=\gamma\frac{A-\alpha P_2(\cos\theta)}{1-(\beta/2)P_2(\cos\theta)}\,, \qquad (1)$$

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$$P_{\perp}(\theta)=\frac{2\xi\sin\theta\cos\theta}{1-(\beta/2)P_2(\cos\theta)} . \qquad (2)$$

A is the integral polarization value (polarization transfer), ξ describes the dynamical polarization, and α and β are the asymmetry parameters for the θ dependence of spin polarization and intensity, respectively.

The effusive barium atom beam was generated in a resistively heated oven. We have chosen barium as the target for our studies, because the low-lying threshold for removal of a $5p$-electron and subsequent Auger electron emission at $h\nu \simeq 21$ eV [17] is readily accessible with a normal-incidence monochromator. Moreover, it is a suitably simple system for a first test of theoretical predictions, since both Ba and Ba^{2+} have a ${}^1S_0$ ground state. This reduces the number of outgoing electron partial waves and causes the anisotropy in the final state to be shared exclusively by the two ejected electrons. Previous studies of the Ba $5p$ subshell using synchrotron radiation and photoelectron spectroscopy were carried out by Kobrin *et al.* [18] and Bizau *et al.* [19]. The ionization process of interest can be denoted by

$$\begin{aligned}\mathrm{Ba}(5p^6 6s^2)\,{}^1S_0 + h\nu &\rightarrow \mathrm{Ba}^+(5p^5 6s^2)\,{}^2P_J + e_P^-(\epsilon s, \epsilon d)\,, \\ &\rightarrow \mathrm{Ba}^{2+}(5p^6)\,{}^1S_0 + e_P^- + e_A^-(\epsilon p)\,, \end{aligned} \qquad (3)$$

where $J=\frac{3}{2}$ or $\frac{1}{2}$ is the total angular momentum of the photoion giving rise to the $O_{2,3}$-P_1P_1 Auger doublet at kinetic energies of 7.5 and 9.5 eV, respectively.

In Fig. 1 we show electron kinetic energy spectra taken at two photon energies where also the spin-polarization measurements were performed. All peaks displayed result from Auger transitions which were discussed by Rassi and Ross [20]. At $h\nu = 23.5$ eV Auger electrons with a maximum kinetic energy of 8.3 eV can be emitted. In the higher resolution electron impact Auger spectra the line at 7.5 eV was observed to be split into two lines [20]. This splitting and the appearance of the other Auger lines in Fig. 1 result from strong $5d$-$6s$ configuration interaction, caused by the collapse of the $5d$ subshell in the presence of the $5p$ hole [19]. With our spectral resolution of $\Delta E \simeq 150$ meV we could not resolve the splitting of the 7.5 eV line; however, calculations [21] revealed that the $(5p^5 6s^2)\,{}^2P_{3/2}$ character is shared by both components with in each case admixtures from the $5d^2$ and $6s5d$ configuration of comparable strength. The spectrum of Fig. 1(a) is recorded at a photon energy between the Ba^+ ${}^2P_{3/2}$ and ${}^2P_{1/2}$ limits where the absorption cross section is increased by more than a factor of 2 due to the influence of spin-orbit autoionization resonances [22,23]. At $h\nu \simeq 23.5$ eV mainly the $(5p^5 6s^2\,{}^2P_{1/2}6d)\,{}^1P_1$ resonance contributes to the absorption spectrum and, weaker, several members of the series labeled c by Connerade *et al.* [23]. The electron spectrum at $h\nu = 25.8$ eV shows in addition the $5p_{1/2}^{-1}$-$6s^{-2}$ Auger line at 9.5 eV kinetic energy. Compared to $h\nu = 23.5$ eV, the typical Auger electron intensities were lower because both the cross section and the photon flux decreased. In this case the ionization process is easier to interpret, since at this photon energy it is dominated by direct ionization and since according to the calculations the Ba^+ ${}^2P_{1/2}$ state is more pure with almost 80% $5p^5 6s^2$ character [21]. The relative intensities of the Auger lines of Fig. 1(b) agree with the results of Ref. [19] at $h\nu = 25.9$ eV.

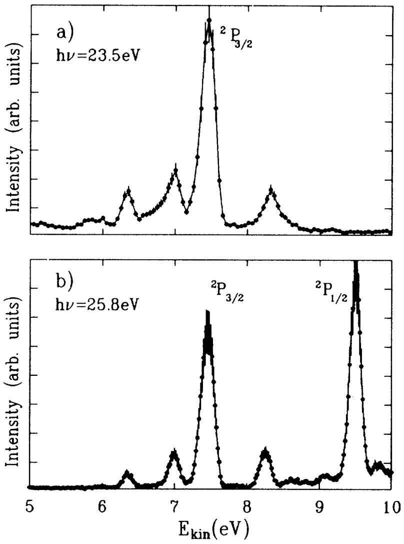

FIG. 1. Electron spectra at two photon energies. The dominant lines are labeled by the quantum numbers of the intermediate photoion state.

In Fig. 2 we show the measured angular distributions of the spin-polarization component $A(\theta)$ for the dominant Auger line at $h\nu = 23.5$ eV and for the $5p_{1/2}^{-1}$-$6s^{-2}$ Auger line at $h\nu = 25.8$ eV. The count rate was typically only 1 Hz or less. The polarization component $P_{\perp}(\theta)$ is not displayed, since the measured values were always lower than 2%, which is compatible with the theoretical value of $\xi = 0$. (Dynamical polarization is a result of the interference of at least two outgoing electron waves and therefore has to vanish for single-channel Auger transitions.) By means of a nonlinear least-squares-fit procedure according to Eq. (1), the values of A, α, and β are determined from these distributions as given as insets in Figs. 2(a) and 2(b). The two angular distributions of Fig. 2 show strong differences in their behavior. The angular distribution of Fig. 2(a) has a large negative value of the parameter A and a weak angular dependence. The distribution for the $\epsilon p_{1/2}$ Auger electrons shows the opposite features. The integral spin polarization is rather small, but the angular dependence of $A(\theta)$ is pronounced and the signs of the polarization parameters are reversed.

For the interpretation of these spin polarization data we use the standard two-step model assuming that the photoionization and the Auger process occur in sequence and that the transition probability of one process is not influenced by the other. (This neglects the fact that in the threshold region a slow outgoing photoelectron and the Auger electron may influence each other by post-collision interaction.) According to the two-step model the connection between the two processes results only from the alignment $\mathcal{A}_{20}$ or orientation $\mathcal{A}_{10}$ of the intermediate excited Ba$^+$ ^2P_J ionic state. The components of the spin polarization vector [see Eqs. (1) and (2)] for Auger electrons have the same analytic form as for photoelectrons. However, the dynamical parameters are factorized into products of the anisotropy coefficients $\mathcal{A}_{10}$ or $\mathcal{A}_{20}$ and the Auger decay parameters β_1, γ_1, α_2, and ξ_2 as defined by Ref. [7] [see Eqs. (4)-(7) below]. Also, only single-channel Auger transitions are possible to a $^1S_0$ final ionic state. For this case, apart from the differential cross section the Auger decay parameters have definite values which do not depend on specific matrix elements but only on the parity and total angular momentum J of the Ba$^+$ ionic state [7]. The photoion orientation can therefore be directly determined from the parameters A and α and—when applicable—also the alignment from the parameter β. As discussed below, we have extracted the orientation coefficients $\mathcal{A}_{10}$ from the angular distributions of Fig. 2. For the $^2P_{1/2}$ ionic state there is no alignment, since $\mathcal{A}_{20}=0$ if $J=\frac{1}{2}$, and the parameters β and ξ both vanish. For the $5p_{3/2}^{-1}$-$6s^{-2}$ line it was not attempted to obtain the alignment directly from the asymmetry parameter β, since the statistical error for the β value was large.

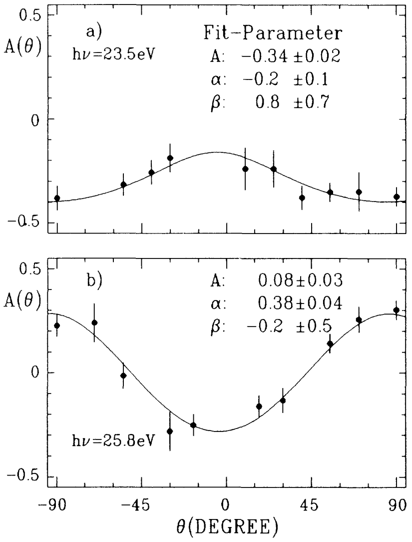

FIG. 2. Measured angular dependence of the Auger electron spin polarization at $h\nu=23.5$ eV for the Auger line with 7.5 eV kinetic energy (a) and at $h\nu=25.8$ eV for the line with 9.5 eV kinetic energy (b). The solid lines represent a least squares fit to the data according to Eq. (1).

According to the theory of Kabachnik and Lee [7] for ionization with circularly polarized light to a $p_{1/2}$ and a $p_{3/2}$ hole state, the anisotropy coefficients $\mathcal{A}_{10}$ and $\mathcal{A}_{20}$ can be expressed in terms of the ratio $\lambda=D_s/D_d$ of the reduced matrix elements for outgoing s or d partial photoelectron waves. The dynamical parameters are then given by

$$\begin{array}{llll} & {}^2P_{1/2} & {}^2P_{3/2} & \\ A=\beta_1\cdot\mathcal{A}_{10}= & \left(-\frac{1}{3}\right)\left(-\frac{1}{2}\right)\frac{1-2\lambda^2}{1+\lambda^2};\ \left[-\frac{1}{3};\frac{1}{6}\right] & \left(\frac{\sqrt{5}}{3}\right)\left(-\frac{\sqrt{5}}{4}\right)\frac{1-2\lambda^2}{1+\lambda^2};\ \left[-\frac{5}{12};\frac{5}{6}\right], & (4) \\ \alpha=-\gamma_1\cdot\mathcal{A}_{10}=- & \left(\frac{4}{3}\right)\left(-\frac{1}{2}\right)\frac{1-2\lambda^2}{1+\lambda^2};\ \left[-\frac{4}{3};\frac{2}{3}\right] & \left(\frac{2}{3\sqrt{5}}\right)\left(-\frac{\sqrt{5}}{4}\right)\frac{1-2\lambda^2}{1+\lambda^2};\ \left[-\frac{1}{6};\frac{1}{3}\right], & (5) \\ \beta=-2\alpha_2\cdot\mathcal{A}_{20}=0 & & 2\frac{1}{20}\frac{1+10\lambda^2}{1+\lambda^2};\ \left[\frac{1}{10};1\right], & (6) \\ \xi=\xi_2\cdot\mathcal{A}_{20}=0 & & 0\,. & (7) \end{array}$$

The numbers in square brackets indicate the limiting values for these parameters. This is a nonrelativistic description, where $\epsilon d_{3/2}$ and $\epsilon d_{5/2}$ waves are not distinguished; for the $^2P_{1/2}$ photoion, however, it is equal to the relativistic result [24]. It is worth noting that information on the photoelectron transition amplitudes is carried over to the Auger electrons via the photoion polarization while phase information is lost. From Eqs. (4),(5) the following relationships for the dynamical parameters can be obtained:

$$^2P_{1/2}\colon\ \alpha=4A,\quad {}^2P_{3/2}\colon\ \alpha=0.4A\,. \tag{8}$$

These relationships may serve to check the validity of the theoretical concepts worked out by several authors [6-8,24]. A deviation from Eq. (8) would show that the Auger process is influenced by the photoprocess.

From the orientation coefficients derived from A and α together the ratios of the reduced matrix elements for outgoing s and d photoelectrons, and also the alignment of the photoion state were determined in turn using Eqs. (4)-(6). For the $p_{3/2}$ core hole at $h\nu=23.5$ eV we obtain $\mathcal{A}_{10}=-0.47\pm0.03$, and from this value $|D_s/D_d|=0.23\pm0.03$ and $\mathcal{A}_{20}=0.07\pm0.01$. Furthermore, within the LS coupling scheme $\beta=2\mathcal{A}_{20}$ holds [see Eq. (6)], giving a consistent result with smaller relative error than the β value listed in Fig. 2(a). Considering these values it should be taken into account that resonant Rydberg states can give contributions and that the Ba$^+$ $^2P_{3/2}$ ionic state contains $5d$ admixtures. The results fulfill the relationships (8), since $\alpha/A=0.6\pm0.3$. Berezhko *et al.* [25] calculated the degree of alignment for a hole state in the $5p_{3/2}$ subshell of Ba$^+$ to 0.28 using a Hartree-Fock (HF) approximation and to 0.32 using a random phase approximation with exchange (RPAE) for a photon energy 0.7 eV above threshold. The value of the HF calculation is closer to our experimental result than the RPAE calculation. However, the theory does not include autoionization. The strongest resonance should increase the D_d amplitude considerably and therefore decrease the ratio λ (and also the coefficient $\mathcal{A}_{20}$) as compared to its value for direct ionization.

Excitation with circularly polarized light even provides data for the ratio $|D_s/D_d|$ for a $\epsilon p_{1/2}$ partial electron Auger wave, where the alignment vanishes ($\beta=\xi=0$), while an orientation of the intermediate state may occur ($A\neq0, \alpha\neq0$). At $h\nu=25.8$ eV, from the angular distribution of the spin-polarization component $A(\theta)$ and from the fit parameters (Fig. 2) we obtain $\mathcal{A}_{10}=-0.27 \pm 0.01$, and it follows $|D_s/D_d|=0.43 \pm 0.01$. The large difference in the ratio $|D_s/D_d|$ for the two cases studied may be due to an increase of D_d caused by the resonance at $h\nu=23.5$ eV. For the $p_{1/2}$ Auger electrons the experimental β value is in accordance with zero ($\mathcal{A}_{20}=0$). The ratio of $\alpha/A=4.8\pm1.8$ agrees with the theoretical value $\alpha/A=4$. With the energy scale shifted by the spin-orbit splitting (1.97 eV), the calculations of Ref. [25] yield for a $p_{1/2}$ hole state $A=0.14$ and $\alpha=0.55$ in the HF calculation, and $A=0.10$ and $\alpha=0.43$ in the RPAE calculation for a photon energy 1.1 eV above the threshold. As might be anticipated, the experimental data ($A=0.08 \pm 0.03$, $\alpha=0.38\pm0.04$) are in better agreement with the RPAE result. For the $5p_{1/2}^{-1}$-$6s^{-2}$ Auger transition at $h\nu=25.8$ eV the resonant contributions may be neglected and the configuration interaction for the intermediate state is smaller; therefore the comparison of experiment and calculation provides a more stringent test of the theoretical description than for the other case.

The results for free Ba atoms discussed here represent a first example of how the spin-polarization transfer to Auger electrons can be used with advantage to analyze the dynamics of a two-step double-ionization process. The angular distributions of the polarization component $A(\theta)$ reflect a substantial orientation transfer from the photoion to the ejected Auger electron. The results confirm the theoretical framework and predictions discussed by Kabachnik and Lee [7]. From the analysis of the Auger electron polarization, it was possible to extract the photoion orientation and the ratio of the reduced photoelectron matrix elements. This was carried out even for a $\epsilon p_{1/2}$ Auger decay where all other dynamical parameters besides the cross section vanish, if the atom is excited with linearly or unpolarized light. The results for these values and the ratios of the spin-polarization parameters are in fair agreement with calculations [25]. Using polarization transfer as a tool, it will be of interest to investigate the Auger decay parameters in more complex cases where several Auger channels are present. Furthermore, it would be desirable to examine the polarization of the corresponding photoelectrons, as well, in order to test the validity of the model in more detail and to study post-collision interaction and related phenomena. Such work is in progress.

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