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Symmetry characterization of unoccupied states in thick alkaline layers by spin-resolved Auger electron spectroscopy using primary excitation by circularly polarized light

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Abstract. CVV Auger electrons emitted from K, Rb and Cs layers are studied using spin-resolved spectroscopy. Oriented 3p, 4p and 5p hole states are excited by circularly polarized radiation in normal incidence. The photon energies range from 12 to 24 eV. With all three materials, the degree and sign of the Auger electron spin polarization vary with the photon energy. As an atomic model of the Auger process predicts, and as a comparison of measurements with the calculated densities of states shows, the spin polarization is essentially determined by the symmetry of the final states reached in the primary (photo)excitation. Just above the excitation threshold, the preferential spin direction of the Auger electrons is measured to be parallel to the spin of the exciting photons corresponding to a predominantly s-like symmetry of the unoccupied final states reached by the excitation. At higher photon energies the preferential spin direction changes to be antiparallel to the photon spin, corresponding to the mainly d-like symmetry of unoccupied states reached by the excitation.

1. Introduction

Auger spectroscopy provides a way for studying the coupling and correlation of electronic states. However, in experiments on non-magnetic materials, only the energetic position and the shape of Auger lines have been analysed so far [1]. The spin polarization of Auger electrons has been measured only with ferromagnetic materials [2–5]. This appears surprising because the theory of AES involves both spin coupling and spin interactions [6–9].

Here we describe an Auger experiment in which the symmetry of the unoccupied states reached by the primary excitation is compared with calculated angular-momentum resolved partial densities of states (partial DOS). In detail we have studied the spin-dependent O_3VV, N_3VV and M_3VV Auger decay in Cs, Rb and K, respectively, following the excitation of oriented hole states by circularly polarized radiation. To compare the measured results with the symmetry properties of the electronic states involved, we describe the excitation and the decay using an atomic model.

2. Experiment

The experiments were performed using the circularly polarized ((90 ± 3)%) off-plane radiation from the 6.5 m normal-incidence monochromator [10] at BESSY with an apparatus

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described previously [11–13]. All data were obtained for the highly symmetric set-up of normal incident light and electron emission within an acceptance cone of ±5° around the surface normal. The photon energies used range from 12 to 24 eV. In this energy range the energy resolution of the monochromator is better than 0.16 eV. A simulated spherical-field 180° spectrometer with an energy resolution of about 500 meV is applied for energy analysis [14]. The electron spin polarization is measured using an UHV Mott polarimeter.

The alkali layers were evaporated onto a clean Pt(111) crystal using dispensers (SAES). The substrate was cooled to about 90 K during the evaporation as well as during the measurements by means of liquid helium. The evaporation of the alkali layers was continued until all signals from the Pt substrate vanished in the standard Auger electron spectroscopy (AES) (Varian CMA with integrated electron gun) as well as in the photoemission. The fresh layers were checked by standard AES and no significant impurities were revealed. LEED has not shown any ordered structures of the layers. During the measurements the base pressure was about 1×10^{-10} mbar. To avoid the influence of the residual gas adsorption the alkali layers were renewed at periodic intervals of about 120 min.

3. Band-structure calculation

The fully relativistic electronic structure calculation was carried out using an alternate full-potential linearized augmented plane-wave (FLAPW) method [15, 16]. Inherent in all APW methods is a subdivision of the unit cell into atomic spheres centred on the atomic nuclei and a residual interstitial region. We have chosen the atomic sphere radii as 2.23 Å for K, 2.37 Å for Rb, and 2.61 Å for Cs. For the exchange–correlation part of the potential we have used the interpolation formula of Hedin and Lundqvist [17]. The charge density of the core electrons has been recalculated in each iteration step. To account for those core-charge tails that extend beyond the atomic spheres into the interstitial region, the np^6 states ($n = 3, 4$ and 5 for K, Rb and Cs, respectively) have been treated like band states. Within the self-consistent procedure the charge density has been calculated by the summation over 285 k-points in the irreducible wedge of the Brillouin zone. The partial DOS refer to the angular momentum decomposition of the band states within the respective atomic sphere.

4. Results and discussion

We assume the CVV Auger process to be a two-step process. This means that the primary photoexcitation and the Auger decay are independent processes. The Auger decay itself can be divided into two additional steps. The first decay step is the refilling of the primary hole by an electron out of the occupied conduction bands (valence band) and the lifting of another conduction band electron, the so-called Auger electron, into an unoccupied conduction band state. Thereby a coupled two-hole state, with a short life span in the alkali layers, is created in the occupied conduction band [1]. The second decay step is the transport of the Auger electrons to the surface and its transmission into the vacuum. We neglect this second decay step because as a result of the normal emission the second decay step is spin independent for high-symmetry low-index surfaces and also for the statistically isotropic (amorphous) materials given here [18]. In the excitation as well as in the decay, core states favouring local interactions are involved. Therefore in the following we shall describe the excitation and the decay in an atomic-like model.

The excitation process follows the relativistic dipole selection rules for $\sigma^+(\sigma^-)$ light: $\Delta l = \pm 1$, $\Delta m_j = +1(\Delta m_j = -1)$. Therefore, starting at the $np_{3/2}$ level ($n = 3, 4$ and 5

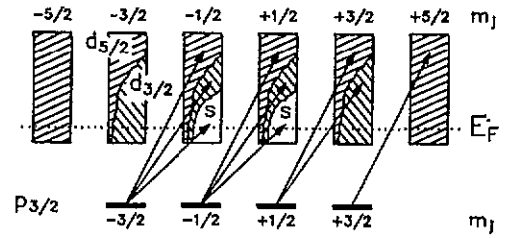

Figure 1. Scheme of the excitation $np^6 + h\nu \rightarrow np^5(n+1)s^1$, $np^5(n+1)d^1$ for σ^+-polarized radiation. The energy differences are not to scale.

for K, Rb and Cs, respectively), only excitations into s and d-like unoccupied conduction band states are possible (figure 1). In the 'simple' alkaline metal, conduction band electrons will screen the core hole [19, 20]. This screening results in a strongly enhanced density of occupied s-like states at the lower edge of the conduction band and an enhanced density of occupied p-like states at the upper edge. Thus, a mainly $np^5(n+1)s^{2-x}p^x$ electron configuration exists locally. In order to simplify this, we restrict the possible decay processes for the present discussion to only that which results in ss two-hole states. In figure 2 a decay scheme is shown, resulting in an ss two-hole state. One of the s-like electrons fills up the core hole and the other will leave the system as the Auger electron. In the Auger decay the electrons involved are coupled by Coulomb interaction. Therefore the parity and the angular momentum J as well as its projection m_J onto the preferential direction are conserved [1, 21–23]. As a result of these conservation rules, the two s-like states, coupled to a singlet state and forming the final two-hole state, determine the symmetry of the outgoing electron state which follows a distinct primary hole state: a hole state $|p_{3/2}, m_j = -\frac{3}{2}\rangle$ will result in an outgoing electron state $|p_{3/2}, m_j = +\frac{3}{2}\rangle$, and a hole state $|p_{3/2}, m_j = -\frac{1}{2}\rangle$ will result in an electron state $|p_{3/2}, m_j = +\frac{1}{2}\rangle$. Primary hole states with positive m_j will result in the corresponding outgoing electron states with negative m_j. If the primary excitations are only transitions into s-like final states, only hole states $|p_{3/2}, m_j = -\frac{1}{2}, m_j = -\frac{3}{2}\rangle$ are excited for σ^+ radiation.

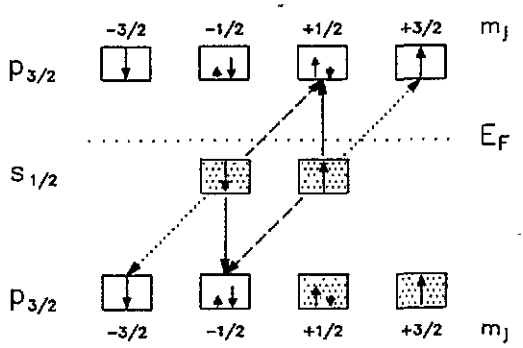

Figure 2. Decay scheme of $p_{3/2}$ holes. Hole states existing before the decay process are given by open rectangles, and the electron states occupied before the decay by dotted rectangles. The different lengths of arrows in the rectangles represent the weight of the spinors $|+\rangle$ and $|-\rangle$. The different types of line at the transition arrows indicate the coupling.

The outgoing electron states are linear combinations of the spherical harmonics Y_{10} and Y_{11} which are proportional to $\cos\Theta$ and $\sin\Theta$, respectively. Θ is the emission angle

measured from the preferential direction given by the spin of the exciting photon. As the experiments were carried out in a normal-incidence normal-emission set-up, the emission angle Θ is $\Theta = 0$. Therefore, only the angular part of the outgoing states proportional to $\cos\Theta$ contribute to the measured intensity. This $\cos\Theta$ term is contained only in the part of the outgoing state $|p_{3/2}, m_j = +1/2\rangle$ connected with the spinor $|+\rangle$. Consequently the Auger electrons should be totally polarized parallel to the photon spin.

Primary hole states $|p_{1/2}, m_j = \mp\frac{1}{2}\rangle$ would behave like the states $|p_{3/2}, m_j = \mp\frac{1}{2}\rangle$. They would result in states $|p_{1/2}, m_j = \pm\frac{1}{2}\rangle$ which in normal emission also yield Auger electrons totally spin polarized parallel or antiparallel to the photon spin, but they are not observable with Cs and Rb owing to a Koster–Kronig transition resulting in $p_{3/2}$ hole states [24, 25].

If, in the primary excitation with σ^+ radiation, d-like final states are involved, hole states $|p_{3/2}, m_j = -\frac{3}{2}, -\frac{1}{2}, +\frac{1}{2}, +\frac{3}{2}\rangle$ and $|p_{1/2}, m_j = -\frac{1}{2}, +\frac{1}{2}\rangle$ are excited. Then, in addition to $|p_{3/2}, m_j = +\frac{1}{2}\rangle$, also the outgoing electron state $|p_{3/2}, m_j = -\frac{1}{2}\rangle$ containing the spinor $|-\rangle$, contributes in normal emission to the measured intensity. From the transition probabilities for the different channels of the excitation from $p_{3/2}$ into only $d_{5/2}$ and $d_{3/2}$ states, a negative Auger electron spin polarization results with a maximum degree of 26%, assuming identical radial parts for the $d_{3/2}$ and $d_{5/2}$ wavefunctions in the LS approximation.

The excitation process depends on the photon energy because the symmetry of the final states reached in the primary excitation varies with varying photon energy. Therefore the Auger electron spin polarization measured as a function of the photon energy is suitable for proving the symmetry of the unoccupied states being reached by the primary excitation. This is of special interest for states with energies between E_F and the vacuum level. For these energies, besides photon absorption processes as used here, the electronic states are only accessible by inverse photoemission and not by direct photoemission.

Figure 3 shows an Auger electron spectrum measured at Rb at a photon energy of (15.4 ± 0.1) eV just above the $4p_{3/2}$ excitation threshold at $h\nu = 14.9$ eV [11, 25–27]. In figure 3(a) a spin integrated spectrum is shown with the Auger peak at a kinetic energy of 11.8 eV and the plasmon loss peak at about 3 eV below. In figure 3(b) the Auger peak is displayed spin resolved. The partial intensities $I_+(E_{kin})$ and $I_-(E_{kin})$ represent the electrons emitted with spin parallel and antiparallel, respectively, to the spin of the exciting photons. The height of the symbols indicates the statistical errors. It is obvious that I_+ is preferred against I_-, i.e. the spin polarization is positive. In figure 3(c) the spin polarization versus kinetic energy is displayed. The spin polarization is calculated from the partial intensities I_+ and I_- by $P = (I_+ - I_-)/(I_+ + I_-)$. Thereby an unpolarized background indicated in figure 3(b) by the straight line is subtracted. Within the limits of the statistical errors the polarization is constant across the peak as shown in figure 3(c) and its average is $(24 \pm 3)\%$. The positive spin polarization is due to the excitation predominantly into s-like final states.

Figure 4 shows measurements to study the dependence of the Auger spin polarization on the excitation process. Thereby the kinetic energy of the Auger electrons is taken at the maximum of the Auger peak and the energy of the circularly polarized light is varied from about 1 eV below the exciting threshold for the outermost $p_{3/2}$ hole states to energies of 5–6 eV above. The resulting constant kinetic energy curves, the total intensity (figure 4(a)) and the spin polarization (figure 4(b)) are compared with calculated s-, p- and d-like partial DOS (figure 4(c)). Therefore two ranges of excitation energies have to be considered.

(1) Only $p_{3/2}$ primary hole states can be excited. As there is only one excitation channel, the spin polarization is a direct measure of the s to d excitation ratio which depends on the ratio of the partial s- to partial d-like DOS. For all three materials near to the threshold, the

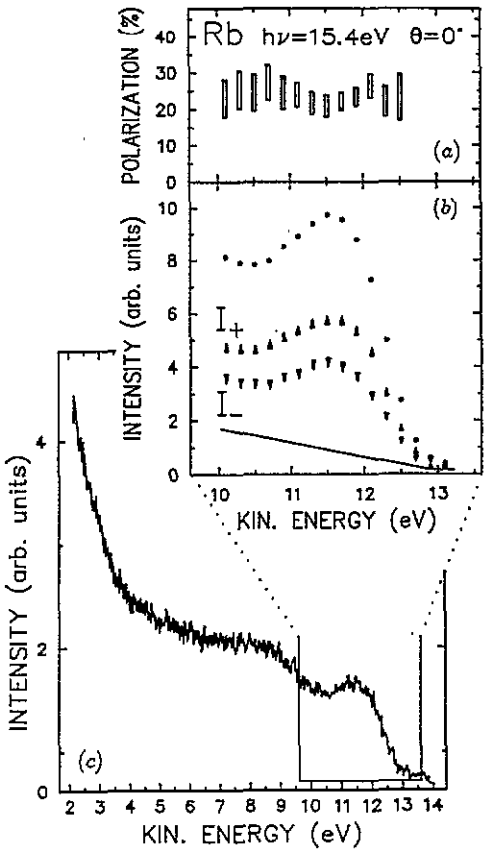

Figure 3. (a) Electron intensity spectrum $I(E_{kin})$ with excitation energy $h\nu = 15.4$ eV. The main structures are the N_3VV Auger peak at 12 eV and the associated plasmon loss peak at about 3 eV below this. (b) Total intensity I, partial intensities $I_+(E_{kin})$ and $I_-(E_{kin})$ of the emitted Auger electrons with spin parallel and spin antiparallel, respectively, to the spin of the exciting photons. The photon energy is also $h\nu = (15.4 \pm 0.1)$ eV. The line at the bottom of the figure shows the unpolarized background intensity considered for evaluation of the Auger electron spin polarization displayed in (c). The heights of the symbols represent the statistical error.

measured Auger electron spin polarization is positive and therefore the s-like partial DOS dominates in accordance with the calculated partial DOS. For Rb and Cs the decrease in the s-like partial DOS and the steep increase in the d-like partial DOS at about 1 eV above the threshold are clearly correlated with the Auger electron spin polarization crossing through zero. Above this zero crossing for Cs, the d-like partial DOS dominates up to the $p_{1/2}$ threshold and clearly results in a negative Auger electron spin polarization.

(2) $p_{3/2}$ and $p_{1/2}$ primary hole states can be excited. The primary excitations of $p_{3/2}$ and $p_{1/2}$ states cannot be separated by selecting the Auger electron kinetic energy. For Rb and Cs, the calculated $p_{3/2}$–$p_{1/2}$ splittings at the Γ point are 0.9 eV and 1.7 eV, respectively, but the primary excitation of $p_{1/2}$ hole states results via a Koster–Kronig transition also in $p_{3/2}$ hole states [24]. For K the calculated splitting of the outermost $p_{3/2}$ and $p_{1/2}$ states is 0.27 eV and that is small compared with the 2 eV width of the Auger peak. The partial DOS shifted by the $p_{3/2}$–$p_{1/2}$ splitting has to be combined with the original partial DOS for

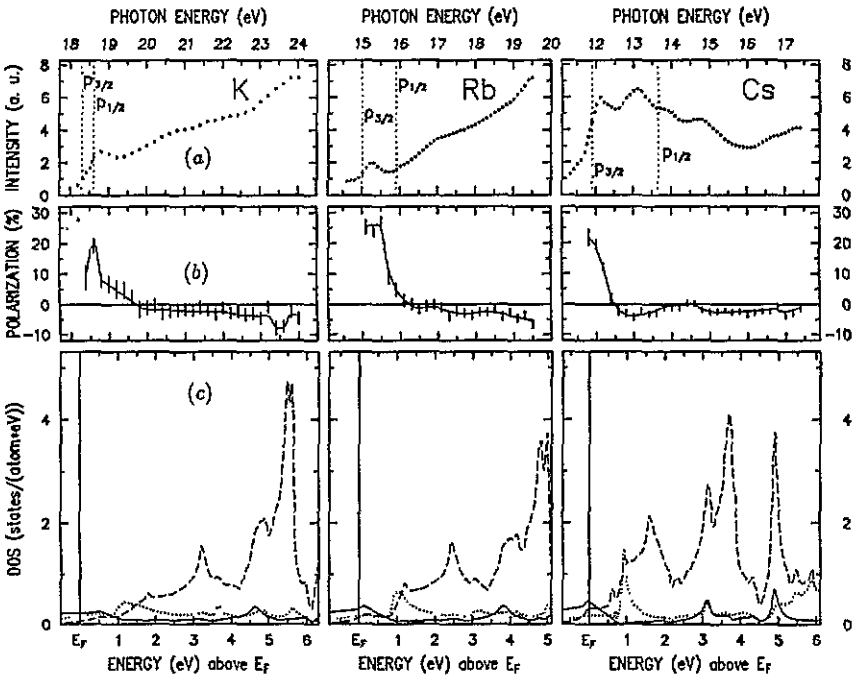

Figure 4. (a) Peak Auger electron intensity versus photon energy for K, Rb and Cs (a.u., arbitrary units). The vertical dotted lines indicate the $p_{3/2}$ and $p_{1/2}$ excitation thresholds. (b) Spin polarization versus photon energy. The error bars represent statistical and systematic errors. A background correction as in figure 3 is applied. (c) Calculated symmetry separated partial DOS, ——, s-like states; ·····, p-like states; – – –, d-like states. The photon energies given contain a monochromator calibration error of ±0.1 eV.

comparing measured and calculated data. For excitation energies above the $p_{1/2}$ threshold, however, the connection between the ratio of the unshifted s and d partial DOS and the Auger electron spin polarization is also obvious. A dominant partial d-like DOS results in a negative Auger electron spin polarization as well as in high Auger electron intensities. From the measured results it is obvious that the measured spin polarization is only weakly influenced by excited $p_{1/2}$ primary holes. For Cs, a very weak peak appears at the $5p_{1/2}$ threshold, but there is no influence on the polarization (the $5p_{1/2}$ threshold coincides with a decrease in the d-like partial DOS). For Rb, the creation of the $4p_{1/2}$ primary hole influences essentially neither the total intensity nor the polarization. (Only for Rb is the change in spin polarization sign accidentally correlated with passing the $4p_{1/2}$ threshold.) For K, the $3p_{1/2}$ excitation is not resolved against the $3p_{3/2}$ excitation in the data given here.

The comparison clearly shows the connection between the s- to d ratio in the excitation process and the Auger electron spin polarization, but the atomic model explains the measured spin polarization only qualitatively. Indeed the measured degree of spin polarization is considerably smaller than the model predicts. At photon energies where almost exclusive d-like final states are reached, we measure a degree of spin polarization with an approximate maximum of 7%. However, on the basis of the atomic model, excitation into only d-like states would result in about 26%.

The reasons for these discrepancies may be as follows.

(i) Disorder in the alkaline layers disturbs the high symmetry assumed to be defined by the normal emission.

(ii) Triplet-coupled conducting band states (sp and pp two-hole states) participate in the Auger decay.

(iii) Exchange scattering between the (hot) Auger electrons and the conduction band electrons depolarizes the emitted electrons.

Reason (i) cannot explain the measured low electron spin polarization just above the threshold, as in the atomic model the averages of the spin polarization of the outgoing electron states $|p_{3/2}, m_j = +\frac{1}{2}\rangle$ and $|p_{3/2}, m_j = +\frac{3}{2}\rangle$ over their population and over all angles will be +88%.

Reason (ii) may have some influence. Two-hole states coupled to a triplet state resulting in different decay channels in the atom-like model could also explain why the measured spin polarization is too small, although the p-like states exist essentially near to the Fermi level E_F. The change in the local DOS due to the screening, however, prefers s states [19, 20]. A dominant contribution of sp and pp components has been found for example for the L_{23} VV Auger process in Si [28, 29] where p-like states dominate the DOS.

Reason (iii) may also be a possibility. Whilst photoemission experiments from Ge with a 20 Å layer of K on top of the surface do not show marked depolarization [30], photoemission from Fe covered with a thick Cs layer points to a considerable depolarization effect [31]. With these Cs data the scattering would reduce the electron spin polarization by a factor of about 0.6. This depolarization would affect the photoelectrons resulting from the primary excitation as well as the Auger electrons. Thus, within the comparison of spin polarization values of both, on the basis of the atomic model, the two exchange scattering processes almost cancel each other out. Reasons (i) and (ii) given above would affect only the Auger electrons. As the atomic model [32] for Cs and especially Rb [33] quantitatively reveals the measured dependence of Auger electron spin polarization on the adjunct photoelectron spin polarization, for Cs and Rb the exchange scattering should be the essential reason for the small Auger electron spin polarization.

5. Conclusions

The measurements clearly indicate the correlation between the measured Auger electron spin polarization and the symmetry of the unoccupied conduction band reached in the primary photoexcitation. It is worth noting that this dependence can be quantitatively explained already in a simple atomic model using the symmetry character of the states. If, in the future, it is possible to calculate the local DOS in the valence band present with the screened core hole and spin-dependent matrix elements, a quantitative comparison between theory and measurements should be possible. Spin-resolved Auger spectroscopy could then become a tool for studying unoccupied states, in particular in the energy region between E_F and the vacuum level, and spin coupling between the conduction band states involved in the CVV Auger process.

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