Core shell electron spectroscopy on high temperature vapors: 2s photoionization and Auger decay of atomic aluminium

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Abstract. An inductively heated, high-temperature evaporation oven for electron spectroscopy is described. Experiments on the synchrotron radiation excited 2s photoionization and Auger decay of open shell Al atoms are presented. The relativistic multiconfiguration Dirac–Fock method has been applied in the theoretical predictions of the spectral structures.

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1. Introduction

Aluminium is one of the most commonly used materials due to its physical properties such as good conductivity, lightweight, inertness, solidity and ease of machinery. Due to the same physical reasons, i.e. low vapor pressure, electron spectroscopic studies of atomic Al as well as many other metals are limited to a few He-VUV source excited outer valence, x-ray excited core shell and electron impact induced diagram Auger experiments. For aluminium, [Ne]3s^2 3p^1 the photoelectron spectra (PES) of valence orbitals and their theoretical interpretation exists (see, e.g. [1]), but until our recent work [2] even the 2p PES and the corresponding Auger electron spectrum (AES) was studied experimentally only by Malutzki et al in 1980s [3]. A few estimates have been presented for the 2s orbital binding energy (see [3]) but so far they have not been experimentally verified, most probably due to the relatively low ionization cross-section and the high temperature needed for evaporation of aluminium. In the present case, the Al vapor was generated using an inductively heated oven system. The idea of the induction heating-based evaporation source in electron spectroscopy has been applied already more than three decades ago (see e.g. [4]). However, due to many reasons like the fear of contamination, the physical size of the generators and the strong oscillating magnetic fields, induction heating has not, to our best knowledge, been used together with modern third generation synchrotron radiation beamlines.

In the present work, we describe the inductively heated evaporation system and synchrotron radiation excited experiments of aluminium 2s photoelectrons and the subsequent Auger decay spectra. The experimental findings are presented together with the ab initio theoretical predictions.

2. Experiments

2.1. Induction oven

The principle of induction heating is in generating eddy currents in the object using a fluctuating magnetic field (see e.g. [5]). The method allows minimized electrical and thermal connections to the heated volume which effectively prevents loss of heating power. Presently, we have produced a modern design of induction heating system for high-temperature electron spectroscopy. The goals for the design have been: low contamination of the experiment, high reachable temperature, rapid heat-up (cool down) and easy transportation.

The constructed oven is presented in figure 1. The water-cooled induction coil tube made of copper is positioned directly around the crucible. The coil assembly is surrounded by a water-cooled nitrogen free stainless steel (SS) cylinder and molybdenum heat shields. The aluminium grains were evaporated using a crucible with three 2 mm diameter holes focused to the interaction point of the set-up. The crucible was placed approximately 1 cm below the interaction region aligning the direction of the holes with the photon beam to provide maximum intensity. The set-up has been found to effectively prevent contamination problems. Due to the well-collimated beam of atomic vapor, a high enough density is still obtained to perform experiments with the available high photon flux and the position sensitive detection system enhancing the detection efficiency compared to conventional narrow exit slit analyzers. The crucible in inductive heating must conduct electricity in order to generate heat by resistive losses of eddy currents. Tungsten was found to be the most suitable crucible material for aluminium due to the high temperature and reactions of liquid aluminium [6]. In the present type of oven,
the heating is concentrated only on a small volume and thus impurities emitted by the heated oven parts are reduced in great extent in comparison to resistive heating systems. Since heat is generated directly in the crucible, it is possible to use high heating power i.e. very high temperatures and minimize the heat-up and cool-down cycles of the set-up. The maximum temperature is limited by the maximum heating power (thermal losses) and the persistence of the crucible material.

Since induction heating generates a magnetic field, it interferes with electrons emitted by the sample atoms. In order to measure interference free electron spectra the heating is pulsed. When the heating is applied, the electron signal from the electron spectrometer is vetoed. By using sufficiently fast pulse width modulated heating power it is possible to keep the temperature stable enough for vapor generation since the crucible acts as a thermal buffer averaging oven temperature. Average heating power is adjusted by varying the relative pulse length of the full 5 kW heating power of our commercial Hüttinger RF-generator\(^2\) compared to constant period of the pulses. In Al experiments a 500 ms sequence was used, consisting of 250–300 ms heating period and 200–250 ms measuring time. The resonant frequency of the RF system was about 260 kHz. The RF-generator is externally controlled by a custom-made control program. Due to

\(^2\) Operating Instructions AXIO, Hüttinger Elektronik GmbH, Elsässer Strase 8, 79110 Freiburg, Germany.
the round structure of the heating coil, the magnetic field is concentrated only at the center of the coil while the radial distribution to outside is very effectively cut down. The same principle is obeyed in the water-cooled RF transportation wires, which are placed very compactly to minimize the spread of the electro-magnetic background. The induction coil in the present version is constructed of ten turns of copper tubing with a continuous flow of cooling water inside the tube. Additional water-cooling is provided for the outer surface of the oven and also to the feedthrough flange.

2.2. 2s electron spectra of Al

The synchrotron radiation excited experiments on Al vapor were performed at the undulator beamline I411 [7] at the 1.5 GeV MAX–II storage ring in Lund, Sweden. A modified Scienta SES-100 electron spectrometer [8] was used to record the spectra of the emitted electrons. In our set-up the original detection system has been replaced with a resistive anode position-sensitive detector (Quantar Model 3394A), which is read via the Quantar Model 2401B position analyzer ADC unit into custom-made spectrometer control software. The detector replacement was done in order to allow fast on–off cycles of the electron counts recording to be used with the induction heating system and to achieve the fast position-sensitive response needed for, e.g. electron–ion coincidence measurements.

The electron spectra of atomic Al were measured at the ‘magic’ 54.7° angle from the polarization vector of the synchrotron radiation, corresponding to angle-independent measurements. The photon energy of 154 eV was used in the measurements of the Al 2s PES. The photon energy was selected to produce the 2s PES slightly below the low energy part of the $L_{2,3}MM$ AES located at about 30–70 eV kinetic energy [2]. Higher photon energies, needed to create the 2s PES above the $L_{2,3}MM$ AES, resulted in an unusable low intensity due to the rapidly decreasing 2s cross-section and beamline flux as well as the reducing transmission of the electron energy analyzer. The binding energy calibration of the PES was obtained by introducing the Kr gas to the interaction region and recording the Kr 3d$_{3/2}$ and 3d$_{5/2}$ photolines at 93.79 and 95.04 eV binding energy [9] simultaneously with the 2s spectrum of Al. The kinetic energy of the AES was calibrated with the aid of the Kr MNN Auger transitions [10].

The 2s photoelectron spectrum shown in figure 2(a) was measured with a 20 eV pass energy of the electron spectrometer corresponding to an approximately 70 meV analyzer contribution to the linewdths. The photon bandwidth was estimated to be 500 meV with the 300 $\mu$m exit slit of the monochromator. The pass energy was chosen to provide well behaved transmission of the analyzer in the kinetic energy region considered. The Auger spectrum (figure 2(c)) was measured using a photon energy of 174 eV and applying the same settings for the electron energy analyzer.

3. Calculations

The calculations of the electronic states involved in the transitions were carried out using the Grasp92 [11] package. In the Grasp92 program the final relativistic atomic state wavefunctions are formed as linear combinations from $jj$ coupled Slater determinantal configuration state functions with the same parity and total angular momentum $J$. The radial wavefunctions are obtained by optimizing the spherically symmetric self-consistent field on the basis of the many-electron Dirac–Coulomb Hamiltonian.
The natural linewidths of the 2s ionized states were experimentally found to be approximately 0.5 eV. Therefore, due to much smaller energy splitting of the fine-structure lines the relative partial photoionization cross-sections were approximated simply by \((2J_β + 1)|\sum_{\nu \alpha} c_{\nu \alpha} \delta_{X_{\nu},X_{\alpha}}|\rho_\alpha\), where \(c_{\nu \alpha}\) are the mixing coefficients of the ground and singly ionized states (see appendix of [12]). \(J_β\) is the total angular momentum of the intermediate state and coefficient \(\rho_\alpha\) the probabilistic density of the corresponding initial state. The relative probability of the 3p → 4p monopole shake-up of the outermost electron during the 2s photoionization was calculated using the so-called sudden approximation, where the shake probability is approximated by the squared overlap integral of the 3p and 4p single electron orbitals in the ground and 2s ionized states, respectively.

The Auger transition amplitudes were calculated by applying the AUGER component of the RATIP package [13]. The AUGER program was developed on the basis of describing the Auger decay as a coherent multichannel scattering state. Comprehensive description of the theory and the program are presented in [14, 15] and references therein.

To describe the configuration interaction and electron correlation properly, the choice of the configuration basis is crucial. In the current calculations, the configurations were chosen so that the most important mixings and Auger decay final states are taken into account, but for simplicity the configuration spaces were kept as small as possible. In the following, the configurations are given using the non-relativistic notation. The ground state is described simply by \([\text{Ne}]3s^23p^1\) configuration and the 2s ionized state by \(2s^1(3p^1 + 4p^1), 2s1^23p^1\) and \(2s^13s^13p^13d^1\) configurations. The Auger final states are described by \(2p^53s^1(3p^1 + 3d^1 + 4p^1), 2p^5(3s^2 + 3p^2)\) and \(2p^6(3s^1 + 3p^1 + 3d^1 + 4p^1)\). Since the \(2p^5n^1l^1l^1n^1l^1\) Auger final states can decay further via cascade-Auger transition, the \(\text{Al}^{3+} (2p^6)\) state was also calculated.

4. Results and discussion

The PES and subsequent AES of atomic aluminium 2s are presented in figure 2 together with the theoretical predictions. Due to the experimental limitations, the 2s PES in figure 2(a) overlapped with the \(L_1\) AES. Thus, for better visualization, the AES, presented in figure 2(c), has been subtracted from the spectrum in figure 2(a) to produce a ‘stand alone’ photoelectron spectrum which is shown in figure 2(b) together with the theoretical prediction. The PES shows two approximately 1 eV wide structures assigned as P1 and P2. The simulated spectra have been aligned to P1 by \(-0.78\) eV offset of the predicted binding energy and convoluted with 0.5 eV Gaussian and 0.5 eV Lorentzian contributions. The Boltzmann distribution of the thermally excited initial states was used in the predictions of the PES with the populations of 37 and 63% for \(^2P_{1/2}\) and \(^2P_{3/2}\), respectively.

The coupling of the 2s vacancy to the outermost single 3p electron gives \(^1P_1\) and \(^3P_{0,1,2}\) states which were predicted to be separated by 0.43 eV in energy. The free fitting procedure of the peak P1 supports the existence of the two lines with the separation of 0.5 eV. The two line fitting procedure suggests 127.4 and 126.9 eV binding energies for the \(^1P_1\) and \(^3P_{0,1,2}\) ionic states, respectively. The structure P2 located at 10 eV higher binding energy than the main line is identified as a monopole shake up of the outermost 3p electron to the 4p orbital during the photoionization process. The shake-up probability was predicted to be 16% of the main transition as the experiment shows about 11% intensity.

Due to the natural linewidth of the photoionized states, the rich fine structure of the AES is smoothed to show only five structures assigned as A1–A5 in figure 2(c). The theoretical
Figure 2. The 2s PES and AES of atomic aluminium. The uppermost spectrum (a) presents the experimental 2s PES measured with the photon energy of 154 eV. The spectrum (b) presents a ‘stand-alone’ PES where the AES measured at the photon energy of 174 eV shown as spectrum (c) is subtracted from the (a) spectrum. The theoretically simulated spectra are presented as dashed line for PES and solid line for AES. The simulated AES has been generated separately for the main PES structure P1 (dashed-dotted) and the satellite structure P2 (dotted). The arrows are drawn to show the deviation of the predicted energy distribution from experiment for peaks A4 and A3.

The prediction describes these structures surprisingly well, thus allowing the identification of the configurations involved in the transitions of the assigned structures. The theoretical simulation in figure 2(c) has been shifted by $-2.8 \text{ eV}$ to match the experiment. The energies and intensities of these linegroups are given in table 1. The highest kinetic energy structures A1–A4 originate from the P1 structure in the PES. It could be expected that the photoionized final state $2s^14p^1$ decays by Auger emission of the outermost electron, however the predicted probability for the $2s^14p^1 \rightarrow 2p^53s^2$ transition is negligible. Unfortunately, in the experiment, the kinetic energy range around 39 eV is covered by a part of the 2p Auger decay [2], but no wide structures were seen in this range. Thus the photoionization satellite structure P2 is interpreted to decay strongly to a $2p^53s^14p^1$ final state which is seen as structure A5 in the AES. In addition to the structures seen in the present kinetic energy range shown in figure 2, the calculations predict that a small part of the intensity of the $L_1M_1M_1$ Auger transitions is located slightly below 100 eV kinetic energy. However these structures were not found in the experimental spectrum in the corresponding kinetic energy region. The calculations also predicted a cascade Auger transition.

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of the \(2p^53s^13p^1\) final states to the \(2p^6\) state in the kinetic energy range 45–50 eV. No additional structures were detected in this range, possibly due to the strong overlap with the \(2p\) Auger structures.

Table 1 shows the final state \(LS\) terms of the most intense Auger transitions involved in structures \(A2–A4\). Due to the strong \(LS\) nature of Al, the understanding of the observed structures and splitting is easier when using the \(LS\) scheme instead of the \(jj\)–coupling used in the code packages. The \(LS\) terms were obtained by taking a unitary transform from \(jj\) to \(LS\) coupled basis. Structure \(A3\) is noted to arise from the transitions to the distinct final state \(2p^53s^13p^12S_{1/2}\). The coupled \(LS\) terms of the final states involved in structures \(A2\) and \(A4\) are noted to be the same. The observed splitting is interpreted to arise from the parallel (\(A4\)) and antiparallel (\(A2\)) spin coupling of the \(3s\) and \(3p\) electrons (\(1P\) and \(3P\) in \(A2\) and \(A4\), respectively). In contrast to the \(3s–3p\), the \(3s–4p\) interaction vanishes completely in the \(2p^53s^14p^1\) final states and only one peak is seen. The trend of decreasing Coulomb interaction with increasing \(n\) quantum number of the outermost electron is expected but the drastic change is surprising. The result can be explained by the unusually large difference between the radial expectation values of \(\langle r(3p_{1/2,3/2})\rangle = 2.3\) au and \(\langle r(4p_{1/2,3/2})\rangle = 5.3\) au. The very diffuse nature of the \(4p\) orbitals also explains the absence of the \(2s^14p^1\) → \(2p^63s^2\) transitions in AES. In addition, coupling of the final state configuration \(2p^53s^13p^1\) also gives high-spin multiplets \(4S\), \(4P\) and \(4D\) which lie on the higher kinetic energy side of the structure \(A2\) approximately at the kinetic energy of 23–24 eV (see the bars in figure (2c)). According to the calculations, the high spin states obtain only about 6.5% of the total intensity, which suggests that Auger decay to the low-spin multiplets \(2S\), \(2P\) and \(2D\) is strongly preferred.

5. Conclusions

The 2s photo and subsequent Auger electron spectra of atomic Al have been presented. The binding and kinetic energies of the PES and AES were given and the structures are interpreted with the aid of relativistic predictions. The experiments presented show that the modern third generation synchrotron radiation sources combined with the appropriate experimental set-up

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are capable of providing information from the electronic transitions in high-temperature vapors with low ionization cross-section. The predictions were seen to be in good agreement with the experiments and the $L_S$-coupled notation was seen to give a formally understandable explanation for the splitting of the Auger structures with the same final state characteristics.

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