Accurate atom–solid kinetic energy shifts from the simultaneous measurement of the KLL Auger spectra for Na, Mg, Al and Si

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Abstract. KLL Auger-energy shifts between free atoms and their solid surfaces were determined from spectra measured simultaneously in identical experimental conditions. Essentially, the shift values obtained for Na, Mg, Al and Si were more accurate than those achieved by combining the results from separate vapour and solid measurements. Using atomic Auger energies and determined shifts, reliable absolute solid state Auger energies with respect to the vacuum level were also obtained. Experimental shift values were also compared with calculations obtained with the excited atom model. 2s and 2p binding energy shifts were estimated from recent high resolution and due to open shell strongly split vapour phase spectra and corresponding published solid state results. Also, the question of the extent to which the 2s and 2p shifts deviate has been discussed here.

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1. Introduction

Binding energy shifts of core levels between free atoms and the same atoms in solid samples are fundamental in solid state theory. One important practical application of experimental shift values comes from recent cluster studies. The size of clusters is often estimated using binding or Auger energy shifts from free atom values [1–3]. The properties of large clusters approach those of solid state and those of small clusters those of free atoms. For these studies, reliable shift values between the ultimate limits of free atoms and solids are crucial. These shift values are often, however, not accurately known experimentally. The main reason for this is that free atom values are measured using gas-phase spectrometers and the vacuum level as the reference energy level, whereas the solid state values are measured applying solid state systems with respect to the Fermi level. In order to bring these values to the common energy scale, solid state values have to be corrected by the work function of the solid sample. The work function values are rather difficult to measure accurately and they depend, for example, on the surface conditions. Thus the obtained shift values contain the inaccuracies of all the three experiments: free atom, solid phase and work function.

In the course of our metal vapour studies, we have developed a simple method for observing simultaneously both the vapour and solid state spectra in identical experimental conditions. The idea is to set a cool needle-like surface into the vapour beam and to observe by a narrow beam slightly hitting the solid needle excited immediate spectra from the vapour around the needle and from the condensed solid surface on the needle at the same time. The electrons that escape from the condensed solid layer and free atoms in its vicinity are at the same potential, determined by the work function of the condensed layer. Therefore the spectra have the same reference energy level and no work function correction is needed.

This simultaneous kinetic energy shift determination method can be applied to both photoelectrons and Auger electrons, giving binding energy and Auger energy shifts, respectively. Photoelectron spectra are currently often measured by intensive synchrotron light, as
are many lower energy Auger spectra. Auger spectra can also be obtained conveniently by electron impact excitation in the laboratory. Thus, it is also possible to create a hole for a deeper core level, which may not be accessible with many low-photon-energy synchrotron radiation beamlines based on grazing incidence monochromators. Practical upper photon energies are usually about 1000 eV for these beamlines, e.g. at MAX II.

We have recently reported results for Sb 4d and Bi 4f binding energy shifts [4]. They are exceptionally interesting because in these special cases molecular species can also be generated in the vapour phase, making possible simultaneous observation of atom–molecule–solid shifts. Very recently, K 2p and Rb 3d shifts were also studied [5]. In this study, instead of concentrating on the binding energy shifts, we concentrate on the KLL Auger energies of Na, Mg, Al and Si. Atomic Auger spectra for these elements have recently been studied with improved resolution, combined with a careful theoretical analysis, by our group [6–8].

2. Origin of the kinetic energy shifts

Electron kinetic energy shifts are often formally divided into initial state chemical shifts and final state extra atomic relaxation contributions. In the homonuclear solid, where atoms are surrounded by identical neighbour atoms, the orbital energy changes in the initial state are small compared to those of free atoms. But if the atom is ionized in the solid environment, the easily movable electronic charge around the hole tends to screen the positive charge of the created positive hole state. This effect is commonly called extra-atomic relaxation due to its extra-atomic character.

The Coulombic screening energy is proportional to the product of the positive charge of the hole state and the negative screening charge. In the case of complete screening, the screening charge around the hole state is equal to the positive charge of the hole. Thus, the interaction energy for the double hole state can be approximated to be about four times the energy of a single charged state. In the photoemission the final state is single charged and the outgoing electron gains extra kinetic energy \( E_x(1 \text{ hole}) \). In the Auger process, the final state is double the hole state with \( E_x(2 \text{ hole}) = 4E_x(1 \text{ hole}) \), but the initial state already has a single hole with \( E_x(1 \text{ hole}) \). The kinetic energy is the difference of the final and initial state energies and thus the extra-atomic relaxation increases in the first approximation the kinetic energy of Auger electrons by \( E_x(2 \text{ hole}) - E_x(1 \text{ hole}) = 3E_x(1 \text{ hole}) \). Thus, the kinetic energy shifts from the extra-atomic relaxation for Auger electrons are roughly three times the corresponding shifts of photoelectrons for metals. For molecules, especially for heteronuclear molecules, initial state chemical shifts also play an important role and must be taken into account. A more accurate theoretical description of the screening effect can be found in [9, 10], where an extended potential model is used and the results are compared with previous shift results for sodium and magnesium.

Due to a roughly three times larger extra-atomic relaxation energy shift than in photoemission, Auger energy shifts may provide a very sensitive and useful method for cluster size studies. Combining experimental binding energy and Auger energy shifts, initial state and extra-atomic relaxation parts can be separated by applying the so-called Auger parameter method [11–13]. For a more detailed discussion on this subject, see, for example, [14] and references therein.

The Auger spectra of open shell atoms are split into several close-lying daughter lines. In this connection, the main Auger lines of open shell atomic spectra are simply treated as
one broader peak representing the intensity-weighted average of the line group and the kinetic energy position of this line is compared with the corresponding solid state main peak.

3. Experiments

The experimental setup for measuring vapour and solid state spectra simultaneously is shown in figure 1. A cool needle is set into the vapour beam. Vapour atoms condensate on the needle, providing a constantly growing clean solid surface in the target region. By shifting the needle, we aim to locate where the excitations by the very narrow beam happen roughly as much from the vapour as from the solid-phase atoms. Due to the much higher atom density in the solid tip, this is a somewhat challenging job, but it can be achieved with patience. By simple potential consideration, it can be shown that the potential variations inside the source volume are less than 10 meV.

3.1. Measurements

Measurements were carried out at the University of Oulu using electron impact for ionization and a Gammadata scienta SES-200 electron spectrometer. In this setup, the electron lens ‘collects’, due to the large magnification of the lens, electrons from a very narrow sample region and focuses them on the entrance slit of the analyser. SES-200 has a hemispherical analyser, which is used as constant pass energy mode changing retardation by the lens voltages. Thus, it scans the wanted energy region without changing the resolution.

The electron lens should have rather constant transmission, but in solid state measurements using electron beam excitation, high intensity of scattering electrons tends to build up electronic charging on the surfaces of lens elements, causing a disturbing electric field inside the system. These fields mostly affect slowly moving electrons, giving a poor intensity for small pass energies. Therefore, we used a high pass energy of 500 eV for all measurements. Electrons were detected with a position-sensitive multichannel plate detector and a high-resolution charge-coupled device camera.

To reach temperatures as high as 1600 °C, induction heating was used. In this method the crucible is placed inside the copper coil, where a high-frequency alternative current oscillates. This induces eddy currents in the crucible, which heat up the sample. To prevent the varying
magnetic field from interfering the electrons during the measurement, heating was gated so that during the short data collection periods heating was off [6].

3.2. Experimental results

3.3. Sodium

Sodium was heated in a graphite crucible and only very slight heating was needed to evaporate it. The experimental KLL Auger spectrum in the kinetic energy region of the KL$^{2,3}$L$^{2,3}$ transitions, excited by 3 keV electrons, is shown in figure 1. The spectrometer entrance slit was 0.8 mm, corresponding to a nominal broadening of 1 eV for 500 eV pass energy.

The spectrum clearly shows both solid and vapour main lines due to the KL$^{2,3}$L$^{2,3}$($^1D$) transitions, where the LS term symbol stands for the coupling of the holes created in the final state of the Auger decay. The main solid state lines at higher kinetic energies (990 eV) are followed by strong plasmon lines (983 eV). The energy difference of 5.7 eV is in very good agreement with the plasmon energy of 5.8 eV published by Steiner et al [15]. A strong solid plasmon peak is also an indication that the solid surface was clean. In order to obtain a good fit, a different background was subtracted from atomic and solid state spectra. Shirley-type background was applied for the energy range of solid state lines and smooth background for atomic lines. The least-square fit gives 13.33 eV for the energy difference of the main solid and vapour Auger lines.

3.4. Magnesium

Magnesium was also heated in the graphite crucible and ionized using 5 keV electron impact. With 0.5 mm entrance slit of the spectrometer and a pass energy of 500 eV, the experimental broadening of 0.7 eV was estimated. Using this value as a Gaussian linewidth and letting the Lorentzian width to change freely, we could get well-fitted spectral lines. Shirley background was subtracted from solid lines and linear background from vapour lines. Figure 2 shows the fitted KL$^{2,3}$L$^{2,3}$ Auger spectrum of magnesium. The fit gives 14.59 eV energy shift to the main vapour solid lines. The plasmon peak of solid Mg is not so pronounced as for Na and is located at 10.9 eV lower kinetic energies just on the right-hand side of the main vapour peak.

Figure 2. Measured KL$^{2,3}$L$^{2,3}$ Auger spectrum of magnesium.
3.5. Aluminium

To measure aluminium, the same settings as for magnesium were used. The only difference was that the BN cup was placed inside the graphite crucible. The temperature needed for proper evaporation inside the crucible was estimated to be 1030 °C and therefore more current was fed to the system. A polynomial line subtracted from measurement points was used for background. Attaching the calculated broadening of 0.7 eV as a Gaussian linewidth we were able to obtain a good fit, with 16.00 eV shifts to main vapour solid lines, shown in figure 3. There should be a plasmon peak at 15.60 eV from the solid main peak, but it is overlapping the main vapour peak and cannot be resolved.

3.6. Silicon

The main difficulties of measuring the silicon KL_{2,3}L_{2,3} Auger spectrum were the high temperature needed, about 1620 °C, and the high reactivity as well as the low ionization cross section of the K-shell electrons. The BN cup inside the graphite crucible also worked well in this case. To gain higher intensity for the main lines, we increased the entrance slit of the spectrometer to 0.8 mm. With a pass energy of 500 eV, it produced experimental broadening of 1.0 eV, which was used as the Gaussian linewidth. The fitted spectrum in figure 4 clearly shows the main vapour solid lines of silicon and gives them the energy difference of 16.4 eV. Again the plasmon peak at 16.9 eV overlaps the vapour peak and cannot be separated.

4. Discussion

4.1. Auger energy shifts

In table 1, we compare our new experimental shift values with the literature values. Atomic Auger spectra were energy calibrated with well-known rare gas spectra with respect to the vacuum level in [6–8]. The kinetic energy scale of figures 1–4 is based on the same calibration. Using the atomic Auger energies and the determined shift values, it is possible to obtain reliable Auger kinetic energies of the studied solids with respect to vacuum level. These values are listed
Table 1. Solid–free atom KLL Auger shifts (eV).

| Element | $\Delta E_A$ | Free atom $E_A$ | Solid (vac.) $E_A$ | $\Phi$ | Solid (Fermi) $E_A$ | $\Delta E_A$ | Thermochem. $\Delta E_A$ |
|---------|-------------|----------------|-------------------|------|-------------------|-------------|-------------------|
| Na      | 13.34       | 977.23         | 990.57            | 2.75 | 994.3$^g$, 994.5$^h$ | 14.32, 14.52 | 16.3             |
| Mg      | 14.59       | 1167.21        | 1181.80           | 3.66 | 1185.1$^i$, 1185.9 | 14.23, 15.03 | 16.2             |
| Al      | 16.00       | 1373.36        | 1389.36           | 4.28 | 1392.9$^k$, 1393.6$^l$ | 15.26, 15.96 | 16.5             |
| Si      | 16.40       | 1595.90        | 1612.30           | 4.85 | 1616.18$^g$, 1616.68$^l$ | 15.43, 15.93 | 17.9             |

$^a$ Measured in this work.
$^b$ Atomic $E_A$ relative to vacuum, measured in Oulu [6–8].
$^c$ $E_A$ of solid relative to vacuum obtained by adding the Auger shift values to the free atom values.
$^d$ From Handbook of Chemistry [20].
$^e$ $E_A$ solid (Fermi) – $E_A$ free atom – $\Phi$.
$^f$ Thermochemical shift estimates [21].
$^g$ Semiempirical $E_A$ of solid relative to Fermi, taken from [21].
$^h$ Steiner et al [22].
$^i$ Carlson et al [23].
$^j$ Attekum and Trooster [24].
$^k$ Dufour et al [25].
$^l$ Wagner et al [26].

Figure 4. Measured KL$_{2,3}$L$_{2,3}$ Auger spectrum of silicon.

in column 4 in table 1. In a previous study [16], Auger energies of solid Zn, Cd, Sn and Pb were also determined relative to the vacuum level.

The observed atom–solid shifts increase smoothly from 13.34 to 16.40 eV in going from Na to Si. Surprisingly, Si also obeys this smooth increasing trend although it is not a metal like the others. The sixth column in table 1 displays Auger energies of solids relative to Fermi level taken from the literature; we show the lowest and highest kinetic energies recorded. The next column in table 1 shows that our new values deviate up to about 1 eV for Na and about 0.5 eV for Si, even from the closer previous shift values determined from separate vapour and solid measurements, and the values scatter a good deal, depending on the literature value. This is clearly too much for a reliable comparison with theoretical results and points to the importance of further accurate determinations. The inaccuracy is also reflected in cluster size determinations, based on the shift values [1–3].
Table 2. The binding energy and Auger energy shifts due to the extra-atomic relaxation calculated using the excited-atom model.

| Element | Ground state 1s-ionized state | Auger final state | Binding energy | Auger energy |
|---------|-------------------------------|-------------------|----------------|--------------|
| Na      | 3s² 1s3s² 2p³ 2s³ 3p³         |                  | 7.18           | 15.64        |
| Mg      | 3s² 1s3s² 3p² 2p³ 3p³         |                  | 6.31           | 17.68        |
| Al      | 3p² 1s3p² 2p³ 3p³             |                  | 7.89           | 20.03        |
| Si      | 3p⁵ 1s3p³ 2p³ 3p⁴             |                  | 9.72           | 22.95        |

Table 3. Solid–free atom binding energy shifts (eV).

| State | $E_b$ atom | $E_b$ solid | $\Phi$ | $\Delta E_b$ |
|-------|------------|-------------|--------|--------------|
| Na2p  | 38.35⁵     | 30.76       | 2.75   | 4.84         |
| Na2s  | 70.84⁴     | 63.5        | 2.75   | 4.59         |
| Mg2p  | 57.64⁶     | 49.59       | 3.66   | 4.39         |
| Mg2s  | 96.55⁵     | 88.7        | 3.66   | 4.19         |
| Al2p  | 81.78³⁸    | 72.68       | 4.28   | 4.82         |
| Al2s  | 127.03³     | 117.8       | 4.28   | 4.95         |
| Si2p  | 108.89⁹    | 99.55       | 4.85   | 4.49         |
| Si2s  | 160⁰       | 149.7       | 4.85   | 5.45         |

a X-Ray Data Booklet [27].
b Handbook of Chemistry [20].
c Krummacher et al [28].
d Shirley et al [29].
e Kammerling et al [30].
f Siegbahn et al [31].
g Jänkkälä et al [32].
h Huttula et al [33].
i Jänkkälä et al [34].
j Partanen et al [35].

The simple semiempirical thermochemical model clearly fails and can only tentatively predict the shifts; for Na the error is as large as 3 eV. The excited atom model overestimates heavily the shift values, especially if the excited electron is placed on the first possible open orbital. The model tends to predict ‘too complete’ screening [17]. This is seen by comparing the experimental values with the predictions shown in table 2. Calculations were performed using the Cowan code [18]. The tendency for increasing shifts as a function of Z is, however, reproduced by the excited atom model, whereas the thermochemical model fails to reproduce this tendency. Calculated shifts decrease if the excited electron occupies higher orbitals, reducing the screening, as is shown in [19]. New accurate experimental shift values are very important for developing the theoretical calculations to obtain better estimates for the shifts.

4.2. Binding energy shifts

In this study, we have not determined by simultaneous observation the binding energy shifts for 1s photoelectrons because these levels are too deep, for example, for soft x-ray beam lines of...
the MAX II synchrotron radiation source. Instead we consider the binding energy shifts based on the published vapour phase and solid values. The atomic 2s and 2p photoelectron spectra are split into many daughter line components due to the coupling of the created hole to the open valence orbitals, whereas the solids show single peaks. In order to compare peak positions, we have calculated intensity-weighted averages for the atoms from the published data. The obtained values and the literature values for corresponding solids are shown in table 3. The table shows that the ratios of Auger shifts to the binding energy shifts are scattered around 3, as is expected in the simple consideration of the magnitudes of the extra-atomic relaxation energies. The shifts of 2s and 2p orbitals are surprisingly close to each other in spite of the fact that 2p is more split due to the open shell coupling.

4.3. Conclusions

KLL Auger energy shifts were found to show an increasing trend in going from Na to Si. This tendency is predicted by the excited atom model even as the ‘full screening’ model heavily overestimates the shift values. Previous separate determinations do not predict any clear tendency and the present and previous shifts differ by up to +1 or −1 eV, which is clearly too much for reliable cluster size determination.

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