be aligned parallel or antiparallel with the spins of the $3d$ electrons of iron.\textsuperscript{13} Thus we observe the $s$-$d$ exchange coupling of the final state. The splitting is a measure of the local magnetic field of $d$ electrons influencing the $s$ level. This process is in fact the smallest magnetometer in atomic size. The material does not have to be ferromagnetic, the only requirement is an unfilled $d$ shell. Hence, XPS can be used to measure the local magnetic moments.

### 8.6 Relaxation Processes

The ionized core level has a finite lifetime before it relaxes back to its ground state. The lifetime ($\Gamma = \hbar/\tau$) is determined by the sum of all mechanisms that makes the excited state relax. The lifetime is very long for atoms, and relatively short for systems with overlapping electron states. Essentially, there are two different relaxation processes, the dipole radiation and electronic recombination, called Auger electron emission.

#### 8.6.1 Dipole Radiation

An electron from a higher state fills the hole, and the energy gained is emitted as a quantum of light. Since this process is a dipole radiation, appropriate selection rules are obeyed:

$$h\nu = E_{B_1} - E_{B_2}$$

$$\Delta \ell = \pm 1$$

$$\Delta j = 0, \pm 1$$

The emission of x-rays is used in research as a spectroscopic tool, in electron microscopy for elemental analysis, and in crystallography for structural analysis.

Figure 8.18 illustrates schematically different x-ray emission processes. For the $K$ series of emission, the initial hole in the $K$ shell is transferred to higher states.

observing the selection rules. The emitted photons are designated as \( K_\alpha \) and \( K_\beta \) series. Using the table for binding energies of elements in Fig. 8.2 we can estimate some frequently-used x-ray transitions. In laboratory XPS measurements mostly Al or Mg anodes are used. The corresponding photon energies can easily be calculated for Al\( K_{\alpha,\beta} \) \( 1560 - 74 = 1486 \text{ eV} \) and for Mg\( K_{\alpha,\beta} \) \( 1305 - 52 = 1253 \text{ eV} \). In XRD experiments mostly a Cu anode is used, because copper conducts the power load in high-intensity sources effectively. The Cu lines are well separated by 20 eV: \( K_{\alpha,\beta} \) \( 8979 - 951 = 8028 \text{ eV} \) and \( 8979 - 931 = 8048 \text{ eV} \). Using Eq. 5.1 we find that these energies correspond to 1.575 Å and 1.541 Å wavelength which are comparable with interatomic distances and hence well suited for XRD work.

The dipole radiation is called the fluorescence. While most of the observed fluorescence lines are normal, certain lines may also occur in x-ray spectra that, at first sight, do not abide to the basic selection rules. These lines are called forbidden lines; they arise from outer orbital levels where there is no sharp energy distinction between orbitals. As an example, in the transition elements, where the 3\( d \) level is only partially filled and strongly interacting with the 3\( p \) levels, a weak forbidden transition (the \( \beta_5 \)) is observed. A third type are satellite lines.
arising from dual ionization. Following the ejection of the initial electron in the photoelectric process, a short, but finite, period of time elapses before the vacancy is filled. This time period is called the lifetime of the excited state. For the elements with lower atomic number, this lifetime increases to such an extent that there is a significant probability that a second electron can be ejected from the atom before the first vacancy is filled. The loss of the second electron modifies the energies of the electrons in the surrounding subshells, and thus x-ray emission lines with other energies are produced. For example, instead of the $K_{\alpha 1,2}$ line pair, a double-ionized atom will give rise to the emission of satellite lines such as the $K_{\alpha 3,4}$ and the $K_{\alpha 5,6}$ pairs. Since they are relatively weak, neither forbidden transitions nor satellite lines have great analytical significance; however, they may cause some confusion in the qualitative interpretation of spectra and may sometimes be misinterpreted as being analytical lines of trace elements.

![Figure 8.19: XRF spectra from an Al-Pd-Mn alloy reveals the local density of occupied states at the site of each alloy component.](image)

The intensity of fluorescence lines depends on the number of holes in the initial state, number of electrons that contribute to the dipole transition, and the dipole matrix elements. For certain transitions, the electrons involved may originate from bands near $E_F$, and their number is related to the DOS. Consequently, an x-ray fluorescence spectrum (XRF) reveals the $\ell$-projected DOS at the atomic site. In an alloy, by tuning the photon energy to the core level energy of the alloy constituents,
we can determine the density of electronic states in the neighborhood of these atoms. This situation is schematically presented for the quasicrystal Al-Pd-Mn in Fig. 8.19.

Figure 8.19 illustrates schematically the emission of x-rays originating from Al, Pd, and Mn atoms in an Al-Pd-Mn alloy. A spectrum around \( h\nu = 118 \text{ eV} \) will reflect the \( p \)-projected DOS of Al atoms, around \( h\nu = 531 \) and \( 559 \text{ eV} \) the \( s \)- and \( d \)-projected DOS at the Pd site, and around \( h\nu = 641 \) and \( 652 \text{ eV} \) \( s \)- and \( d \)-projected DOS at the Mn site.

X-rays are not effectively absorbed at air. Hence XRF experiments do not require high vacuum conditions especially so if the initial hole is created by x-rays. Therefore, XRF is well suited for elemental analysis of technical alloys and widely used in industrial applications. We have to bare in mind that the method is not surface sensitive.

The emission of characteristic x-rays is also used in SEM as described in Section 3.2.3 in order to identify the elements in the specimen which is currently been imaged. The method is widely referred to as EDX or EDAX.

### 8.6.2 Auger Electron Emission

The intensity of electromagnetic radiation depends on the dipole interaction between the hole state and the state of the electron that fills the hole. This quantity depends on the energy difference between the two states and hence on the atomic number \( Z \) squared. It follows that the probability \( \omega_R \) for radiation depends on \( Z^4 \).

![Figure 8.20: Dependence of the fluorescence yield (shaded area) and Auger yield (white area) on atomic number. Ref. [14].](image-url)
Another process following a core excitation is of purely electronic nature. It is a redistribution of electrons and holes resulting in emission of an electron. This radiationless process is called Auger electron emission after Pierre Auger (1899 – 1993). He observed electrons with constant kinetic energy emitted from Ar\(^+\) ions. This process occurs between electronic shells and depends on the overlap of the shells and hence governed purely by Coulomb interaction. This interaction is effective at the atomic site where the hole is located and depends on \(e^2/r\). The probability for Auger electron emission is \(\omega_A\). The Auger process transfers the holes from states with higher \(E_B\) to those with lower energy. In the radiation process the initial and final states both are hole states, while in the Auger electron emission the initial state is a hole state and the final state has two holes.

The initial hole state is bound to relax and hence the sum of the probabilities \(\omega_A\) and \(\omega_R\) is unity. \(\omega_R\) depends on the nuclear charge \(Z\) in the fourth power.\(^{14}\) Figure 8.20 shows the \(Z\) dependence of the fluorescence yield. It is obvious that for lighter elements like C or O, \(\omega_R\) is negligibly small which makes detection using EDAX extremely challenging. For the light elements Auger electron emission dominates, as indicated by the white area.

If the system survives in a quantum state for a time $\tau$, in this case the initial hole state, the energy of the quantum mechanical system in principle cannot be determined with accuracy better than the spontaneous decay $\Gamma \approx \hbar/\tau$. This is fundamental uncertainty relation for energy. In principle, no excited state has infinite lifetime $\tau$, thus all excited states are subject to the lifetime broadening $\Gamma$. The shorter the lifetimes of the states involved in a transition, the broader are the corresponding spectral lines. As seen in Fig. 8.21, $K$-shell broadening of some heavy elements is so large that the ionization of these levels cannot be detected. In general, the lifetime of an ionized state is short if there are several electronic states with smaller $E_B$ which can fill the state. These channels are numerous for heavy elements.

For slow Auger processes, i.e., long life time of the ionized state, we can treat the ionization and relaxation process separately. If, on the other hand, the hole state is filled by an electron of the same shell, with the same principal quantum number $n$, the probability $\omega_A$ becomes very high owing to the strong overlap of the wave functions. The relaxation process is then very fast and is called the Coster-Kronig (CK) transition. Thus, CK transition instantly transfers the hole state to subshells with lower $E_B$ and displays a very broad spectral width. If all three states involved in the relaxation process originate from the same shell, we have a super-Coster-Kronig transition with a still higher probability, and we cannot sort out the ionization and relaxation processes from each other because of the fast time scale.

Figure 8.22: Auger and Coster-Kronig transition in phosphorus. Unknown report.

Figure 8.22 shows the intensity of the $L_{2,3}$ relaxation as a function of the excitation energy in phosphorus. When the energy is sufficiently high to ionize the $L_1$ shell around 190 eV, the $L_1$ hole state is transferred to $L_{2,3}$ shells via a CK process, as shown the energy diagram on the right-hand side, and the probability
\[ \omega_A \] grows markedly. In order a CK process can take place, the energy difference between the \( L_1 \) and \( L_{2,3} \) shells must be larger than the energy necessary to excite an electron from the valence band to vacuum. Hence, the CK process is not always energetically possible.

The kinetic energy of Auger electrons is characteristic of the emitting atom and is well suited for elemental analysis. Yet, the exact energy value of the transition depends on several relaxation mechanisms. The *intraatomic relaxation* is a term associated with the redistribution of charge before the Auger process takes place. So, it is the response of the system to the creation of the hole state. In cases where the transitions are so fast that the *spectator electrons* cannot react, *sudden approximation* (= *frozen-orbital approximation*) is applicable and Koopmans’ theorem may be used: \( E_B = -\epsilon_i \). Relaxation of the system is taken negligible.

On the contrary, if the hole state lives long, the spectator electrons can reorganize in energy. This situation is referred to as *equivalent-core approximation* (= \( Z + 1 \) approximation). This is the *adiabatic limit* with \( E_B = -\epsilon_i - \Delta E_{\text{relax}} \). The estimation of \( \Delta E_{\text{relax}} \) is not straightforward, it changes from element to element, compound to compound. One usually considers besides the intraatomic relaxation the *extraatomic relaxation* which describes the screening of the final-state holes.

The Auger transition takes place between electron shells with well-defined binding energies. As a result, Auger electrons have a definite kinetic energy characteristic to the element in which the hole state is created. Thus, the measurement of the kinetic energy of Auger electrons serves as a tool for chemical analysis of the surface. The method is surface sensitive owing to the limited mean free path of the emitted electrons, given in Fig. 1.14. The emission intensity, on the other hand, is a measure for the concentration of the element in a near-surface region.

\[ \begin{align*}
\text{Intensity (arb. units)} & \quad \text{Al-Pd-Mn clean} \\
\text{Electron energy (eV)} & \quad \text{Ep = 2.4 keV}
\end{align*} \]

Figure 8.23: Auger transitions in the quasicrystal Al-Pd-Mn. M. Erbudak, unpublished.
Figure 8.23 shows an Auger spectrum from a clean $\text{Al}_{70}\text{Pd}_{20}\text{Mn}_{10}$ quasicrystal surface. The sample is excited by 2.4-eV electrons, and the backscattered electrons are energy analyzed. The signal is electronically differentiated in order to detect the Auger signal without excessive noise due to the strong background. The main signal around 70 eV reveals the Al component, while the structure around 360 eV is due to Pd. Mn signal is less intense and is distributed between 600 – 700 eV. Similar spectra are used during the cleaning process of the sample surface that shows around 280 eV carbon and 520 eV oxygen signals due to contamination. One continues the cleaning process until these signals disappear.

![Diagram of Auger spectrum](image)

Figure 8.24: The film B is vacuum deposited on the substrate A. If the growth is homogenous, known as FV growth, we expect an exponential dependence on the thickness $d$ of the Auger signal for both elements. The broken lines point to a layer-by-layer growth. The Auger signal increases linearly within a film until the film is completed.

Epitaxial growth can be monitored using Auger electron spectroscopy, as illustrated schematically in Fig. 8.24. In homogenous growth of the layer B on the substrate A, the Auger signal from the substrate decreases exponentially, $I_A \propto e^{-d/\Lambda_B}$, and the signal from the film material grows as $I_B \propto (1-e^{-d/\Lambda_B})$ as the film thickness $d$ increases. $\Lambda_B$ the mean free path of electrons in the film B.

Because of the high energy and high brightness of the incident electrons, high-quality Auger electron spectra can be acquired with extremely high signal-to-noise ratios. Figure 8.25(a) shows a high energy resolution Auger electron spectrum of clean silver nanoparticles supported on a small MgO crystal; the silver MNN doublet is clearly resolved. Figure 8.25(b) shows the corresponding oxygen KLL Auger peak from the same specimen area.\textsuperscript{15} Surface compositional analysis of individual nanoparticles is essential for understanding the activity and selectivity of industrial bimetallic or multi-component catalysts used in a variety of chemical processes. Because of the high-surface sensitivity of Auger electrons, it is possible to determine qualitatively and, in some cases, quantitatively, the surface composition of nanoparticles consisting of multiple components. High spatial resolution Auger

electron spectra can provide information about the surface enrichment of specific elements and information about how this enrichment varies with the size of the nanoparticles.

![Auger electron spectra](image)

**Figure 8.25**: Auger electron spectra of (a) Ag MNN and (b) O KLL peaks of an Ag/MgO model catalyst. Auger maps of silver and oxygen are shown in (c) and (d), respectively. Ref. [15].

The primary-electron beam used to induce Auger transitions can be scanned on the surface to produce spatially-resolved chemical information. The resolution is determined by the size of the focused beam and to a certain extent by the interaction volume of electrons in a near-surface region of the sample. Yet, for some samples, an image resolution $< 1$ nm can be achieved in scanning Auger microscopy. Such Auger maps have received great popularity, because the experiment is easily combined with several others. Silver nanoparticles $< 1$ nm in diameter and containing as few as 15 silver atoms have been detected. Figures 8.25(c) and (d) show, respectively, Ag and O maps of an Ag/MgO model catalyst, clearly revealing the high-spatial resolution of Auger elemental maps. The resolution in images depends on several sample- and instrument-related effects. The sample-related effects include: (i) surface topography, (ii) escape depth of the collected Auger electrons,
(iii) contribution from backscattered electrons and (iv) localization of the Auger electron generation processes. The last factor sets the ultimate resolution limit that will be achievable in images. Since the primary inelastic-scattering processes involve excitation of inner-shell electrons, the generation of Auger electrons is highly localized. With thin specimens and high-energy incident electrons, the contribution from backscattered electrons should be negligible; it may, however, degrade the image resolution and affect the image contrast of bulk samples. The instrument-related effects include: (i) the intensity distribution of high-energy electron probes, (ii) the collection efficiency of the emitted Auger electrons and (iii) the instability of the microscopes. In a modern instrument, the instrument-related factors set the limits of obtainable resolution to \( \sim 1 \) nm in Auger peak images of thin specimens. The minimum detectable mass in high spatial resolution images is \( < 3 \times 10^{-21} \) g.

The Auger transition is a local process, because the driving force is the hole state localized at the atom. The process leaves behind the atom in a two-hole state. The interaction of these holes determines the line shape of the emission spectrum. For quasi-free Bloch states participating in the Auger transition, the Coulomb repulsion can well be neglected. As a result, the line shape for such a CVV transition, where \( C \) stands for a core state with the initial hole and \( V \) for valence band, corresponds to a self-convolution of the DOS in the valence band. Further, the initial hole is well screened in metals with Bloch states and lowers the total energy of the excited state. This is not the case in atoms. Surfaces behave in between.

![Figure 8.26: Progressive symmetry breaking for the final L shell configurations in KLL transitions. Ref. [16].](image-url)
On the contrary, the line shape of a CCC Auger transition is determined by the type of interaction of the two-hole state. We differentiate three principal cases:\(^{16}\)

a. In the light elements, the Russel-Sounders coupling (Coulomb) dominates.

b. For the heavy elements, mainly spin-orbit (\(jj\)) coupling is observed.

c. Intermediate coupling is relevant for elements in between.

The relative energy splitting of each multiplet caused by these mechanisms is illustrated in Fig. 8.26. Far left, for light elements, energies are completely degenerate with nuclear Coulomb potential. There is no electrostatic interaction between electrons and no spin-orbit interaction. Thus, \(n\), \(l\), and \(s\) are good quantum numbers. As elements become heavier, electrostatic interaction has to be considered between electrons, resulting in states of different total orbital angular momentum \(L\). Splitting into triplets and singlets due to exchange interaction occurs, and the effect of spin-orbit interaction results in five allowed final states in pure \(LS\)-coupling (the triplet \(3P_{0,1,2}\) belonging to the \((2s)(2p)^5\) configuration is degenerate in this limit). In the intermediate coupling we have nine allowed final states. Far right, for the heavy elements in the limit of \(jj\)-coupling, six allowed final states are presented.

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Krypton atom falls into the intermediate region, as illustrated in Fig. 8.26. The Auger spectrum recorded from Kr gas is depicted in Fig. 8.27 for the relevant energy region. In gases the electronic interactions between the excited state and the rest of electrons are extremely week and the final state lives very long. Hence the lifetime broadening is negligible and each final-state multiplet is well resolved as seen in the figure.\(^{17}\)

![Figure 8.28: Experimental $LMM$ Auger-transition spectrum from Cu. F. Vanini, unpublished.](image)

Some filled shells in common metals may also behave like core levels, such as the $3d^{10}$ electrons of copper located near $E_F$. Fig. 8.28 shows the Auger $LMM$ transitions in Cu metal. We observe that the Auger spectrum is dominated by final-state multiplets, this time the final $3d^8$ state. The $L_3M_{4.5}M_{4.5}$ components are located near 920 eV, while the $L_2M_{4.5}M_{4.5}$ multiplets are observed near 940 eV. By inspection, we can state that among the possible multiplets, $^3F_4$ is the Hund’s-rule ground state. This means that the emitted electrons leave the Cu atom in the least excited state and hence they have the highest kinetic energy. This transition is denoted with an arrow for the $L_3M_{4.5}M_{4.5}$ group in the figure.

\(^{17}\)L.O. Werme et al., Physica Scripta 6, 141 (1971).