<u>Chapter 1.</u> Theoretical Background

1.1 Photoemission

Photoemission is based on the photoelectric effect, being one of the most used experimental techniques for gaining information on the electronic structure of materials. The sample is irradiated by photons (ideally highly monochromatic) and the emitted electrons are analyzed with respect to their kinetic energy (and to their direction of propagation in angular resolved photoemission). When photons in the ultraviolet spectral range are used, the technique is called UV photoelectron spectroscopy (UPS). When X-rays are used for excitation, the technique is called X-ray photoelectron spectroscopy (XPS) or ESCA (Electron Spectroscopy for Chemical Analysis). Nowadays, the availability of synchrotron radiation allows the use of a wide spectral range of excitation energies.

In photoemission experiments on solids, only electrons originating from a thin surface layer of the sample are normally used in the analysis of the spectra, which makes photoemission a surface sensitive technique. The reason is that only the electrons which leave the sample without loosing energy are carrying information about the electronic structure directly. The probability for an electron to leave the sample without inelastic scattering is given by the mean free path or electron escape depth. The electron escape depth is a function of the electron kinetic energy, being only in the order of a few Å. The large number of electrons which undergo inelastic scattering processes form the secondary electrons background in a photoemission spectrum.

In a PES experiment, the photocurrent results from the excitation of electrons by the electromagnetic field from the initial state i (with wave function ψ_i) to the final state f

(with wave function ψ_f). Considering H_0 the Hamiltonian of the solid in the ground state and the ionizing radiation field as a perturbation H', the transition probability per unit time is given by Fermi's Golden Rule

$$R = \frac{2\pi}{\hbar} \left| \left\langle \psi_f \left| H' \right| \psi_i \right\rangle \right|^2 \delta(E_f - E_i - \hbar\omega).$$ E 1.1-1

In the dipol approximation the perturbation can be expressed as

$$H' = \vec{E} \cdot \vec{D}$$ E 1.1-2

where $\vec{E}$ is the external electric field and $\vec{D}$ is the dipol moment.

For the interpretation of the photoemission process, the so-called 'three-step model' [BeS64] was proved to be useful [Lüt93, Hüf95]. In this model the photoemission process is separated into three incoherent steps. In a first step the photon is absorbed and the excitation of the electron takes place. In a second step this electron passes through the sample to the surface. In the third step the electron escapes through the surface into the vacuum.

A more rigorous theoretical approach to the photoemission process is given by the 'one-step model' [Mah70]. This model considers the excitation from an initial state (Bloch wave in the crystal) into a damped final state near the surface. This damping takes into account the short mean free path of the electrons in the solid.

In most of the theoretical treatments of photoemission, an infinitely short time for the removal of the photoelectron is assumed, this being referred to as the sudden approximation. The time for the photoemission process depends on the velocity of the escaping electron and therefore the sudden limit is best suited for high excitation energies [MaN95]. Actually the sudden approximation becomes exact in the limit when the kinetic energy of the emitted electron is infinite for isolated systems such as atoms or molecules. In the case of solids the electrons come from a surface region and the mean free path is an essential parameter of the process, thus the sudden approximation is never exact, not even at high energies [HeL2001]. With increasing electron energy the mean free path increases and the electrons come from increasingly larger distances from the surface. Thus the sudden approximation should be corrected always for extrinsic losses [HMI98]. In the case of an interacting N-electron system, the sudden approximation assumes that the photoelectron is decoupled from the (N-1)-electron state and therefore doesn't carry information about it [KeR2001].

The absorption of a photon with energy $h\nu$ causes the excitation of an N-electron system which is described by the initial state wave function $\psi_i(N)$ with energy $E_i(N)$ into a final state ion characterized by $\psi_f(N-1,k)$ with $E_f(N-1,k)$ plus a photoelectron with kinetic energy E_{kin}; k denotes the initial level from which the electron was removed. Thus the conservation of energy is described by

$$E_i(N)+h\nu = E_f(N-1,k)+E_{kin} \qquad\qquad \text{E 1.1-3}$$

and the binding energy with respect to the vacuum level is expressed as

$$E_B^{V}(k)=E_f(N-1,k)-E_i(N). \qquad\qquad \text{E 1.1-4}$$

If it is assumed that the remaining (N-1) electrons have the same spatial distributions and energies in the final state as they had in the initial state before the emission of the electron (frozen-orbital approximation), then the binding energy equals the negative orbital energy of the emitted electron.

$$E_B^{V}(k)_{K.T.} = -\varepsilon_k. \qquad\qquad \text{E 1.1-5}$$

This approximation is the Koopmans' Theorem [ErK85]. This theorem is not exact because it neglects relaxation of the remaining electrons and also relativistic as well as correlation effects. Hence, in a better description these terms should also be taken into account.

Within the sudden approximation an important 'sum rule' can be derived. It states that the average of the binding energies for several peaks at $E_B(k)$, which are associated with a primary excitation, multiplied by their respective intensities I_k, is equal to Koopmans' theorem binding energy $-\varepsilon_k$:

$$-\varepsilon_k = \sum_k I_k E_B(k)/\sum_k I_k. \qquad\qquad \text{E 1.1-6}$$

Thus, in the sudden approximation, Koopmans' energy corresponds to the center of gravity of the entire spectrum including the satellites [MaN95].

A different approach used in treating the photoemission process is represented by the adiabatic approximation. The adiabatic approximation is approached in the case of threshold ionization of a certain electronic level. Generally this applies for low kinetic energy of photoelectrons. In the adiabatic limit the photoelectron is assumed to leave the system slowly so that the electrons from or near the excited atom change their energy by

slowly adjusting to the effective atomic potential in a self-consistent way [SJR83]. Thus, at any instant, the system is in a state of equilibrium. The correlation between the photoemitted electron and remaining atomic electrons is very strong in the case of an adiabatic transition [Tho84].

In photoemission it is difficult to strictly define criteria for the applicability of the sudden versus the adiabatic approximation for a given process. The energy range in which one or the other approximation should be used is not well defined. Theoretical but also experimental work has been dedicated to the estimation of the kinetic energy limit of the photoelectron at which the sudden approximation becomes accurate. Some of these studies concerning the transition from the adiabatic to the sudden limit are reviewed by Hedin et. al. [HeL2002]. It was found that for a weakly correlated system, like an sp-metal or a semiconductor the sudden limit in core electron photoemission is approached very slowly, on the keV scale [HMI98]. For strongly correlated systems (such as certain transition metal and rare earth compounds, high T_c compounds, chemisorption systems) the sudden approximation is, contrarily, reached quickly for small kinetic energies of the photoelectron. In the case of N_2 adsorbed on Ni(100), at the ionization of N1s level, the transition from adiabatic to sudden excitation was found to be abrupt and to occur within approximately 15 eV [SJR83]. Thomas [Tho84] has confirmed this theoretically. Calculations also showed a rapid approach of the sudden limit, within 5-10 eV, when parameters relevant to copper-dihalide compounds were used [LGH99, HeL2002].

Resonant Photoemission

An elegant method of identifying the character of certain features in the valence band spectra is to employ resonant photoemission techniques. Photoemission resonances are closely related to intra-atomic transitions and thus enhancements of photoemission features of a certain element often occur at an absorption edge for the respective element.

By scanning the photon energy across a particular absorption threshold, observed enhancements (and occasionally reductions) of the intensities of particular features in the valence band spectra are detected. In the case of a true resonance process, these enhancements are due to the coherent superposition of the directly photoemitted electrons with Auger electrons which result from the decay of the core hole following the resonant excitation. In other words, in resonant photoemission, the same final state of the system is reached at the direct photoemission and by Auger decay. The Auger process represents an element-specific local probe and thus the intensity variations of certain photoemission features can be used to discriminate contributions of different elements in the valence-band

spectra [MWK97, Lau98, MKN99]. Moreover, since photoemission resonances imply the presence of localized holes, information about the unoccupied states close to the Fermi energy can be extracted using this method [LSS90].

The intensity of the feature in the photoemission spectra which experiences a resonant enhancement, i.e. for which the direct photoemitted electrons interfere with the Auger electrons, is not simply the sum of intensities of the individual subprocesses. The amplitudes of the different processes have to be added coherently. The resulting intensity as function of the photon energy may be described by the so-called Fano lineshape [Fan61]

$$N(\hbar\omega) \cong \frac{(\varepsilon + q)^2}{\varepsilon^2 + 1}, \qquad \varepsilon = \frac{\hbar\omega - \hbar\omega_j}{\Delta(\hbar\omega_j)/2}. \qquad \text{E 1.1-7}$$

In this equation (E.1.1-7) $\hbar\omega$ represents the photon energy, $\hbar\omega_j$ is a photon energy equal to the binding energy of the core level near which the resonance is studied, q is a parameter for the particular core level, and $\Delta(\hbar\omega_j)$ is the full widths at half maximum of that core level. Thus the photoemitted intensity has a characteristic dependence on the photon energy with a strong enhancement at the crossing of the absorption edge of a core level, preceded by a dip and followed by a clear decrease. The shape of the Fano profile is strongly influenced by the parameter q. The square of this parameter is proportional to the ratio between the strengths of the core level assisted (autoionization) process and the strength of the direct photoemission over the core-hole widths [MWK97].

Another characteristic for resonant photoemission is the fact that the kinetic energy of the spectral feature which is resonantly enhanced disperses linearly with photon energy [MWK97, GCP2000]. Especially in the case of solid samples, this might be a very useful additional criteria for establishing whether the intensity increase of a valence band feature is truly resonant or not.

A great benefit for the development of photoemission and, in particular of resonant photoemission, has been the availability of synchrotron radiation, especially of third generation synchrotron sources. Synchrotrons provide photon energies extending from the infrared region up to hard X-rays. The tunability of this radiation is one of the properties most intensively exploited and opens tremendous paths for a fundamental understanding of the electronic structure and properties of materials. Synchrotron radiation is strongly collimated, high enough photon fluxes from undulators allowing for high-resolution measurements. High photon flux is also the main requirement in photoemission spectroscopy especially because the photoionization cross section of most orbitals

decreases with increasing excitation energy. Finally it should be mentioned that the well-defined time structure of synchrotron radiation is a result of the high-frequency acceleration of the electrons (500 MHz at BESSY II, Berlin). Recently, experiments combining certain laser sources with synchrotron radiation were performed (for review of some studies of this type see e.g. [Hai95, GBH95, MTH97, QBW98]). The development of third generation synchrotron sources, which provide pulses in the order of 30 ps, opens the possibilities of investigating fast dynamical processes in a pump-probe type experiment.

All these properties, combined with the fact that synchrotron radiation is polarized, allow for complex experiments and make synchrotron radiation one of the most important tools for the investigation of matter.

1.2 Satellites in Photoemission Spectra

Atoms, molecules and solids are many-electron systems in which the electrons interact via Coulomb and exchange interactions.

In the sudden approximation the ionization process is assumed to be very rapid, and due to the primary photoionization, a system may suffer multielectron excitations [SJR83]. During the primary photoionization other electrons can be excited to higher-lying bound states (shake-up process) and the corresponding lines in the spectrum, appearing at higher binding energies, are called shake-up satellites. In the case of metals, the shake-up processes are also manifested by the existence of asymmetric core line shapes. If the excitation occurs into free continuum states, leaving the atom in a doubly ionized state, the effect is denoted as shake-off process. For solids, the shake-off satellites do not appear in most of the cases in the spectrum as distinct peaks because they usually fall into the energy region of the inelastic secondary electrons [ErK85].

Sometimes satellites are also observed on the low binding energy side of the main peak. These are the shake-down satellites. In a solid sample, at direct photoemission, they can originate via filling of a previously unfilled level that is pulled down below another filled level in the presence of a core hole. The lower binding energy of the shake-down satellites compared to the main line is due to improved screening of the core hole as a result of the shake-down process.

All these satellites are final-state effects, being a result of the created hole and of the excited electron.

Satellites in Photoemission Spectra of Divalent Copper Compounds

Special attention in the photoemission experiments was paid to the study of copper containing compounds. Among them, Cu_2O and CuO were considered as models for compounds in which the copper is formally monovalent, respectively divalent, and therefore a large amount of theoretical and experimental work was done on those materials [GTE88, KGJ2000].
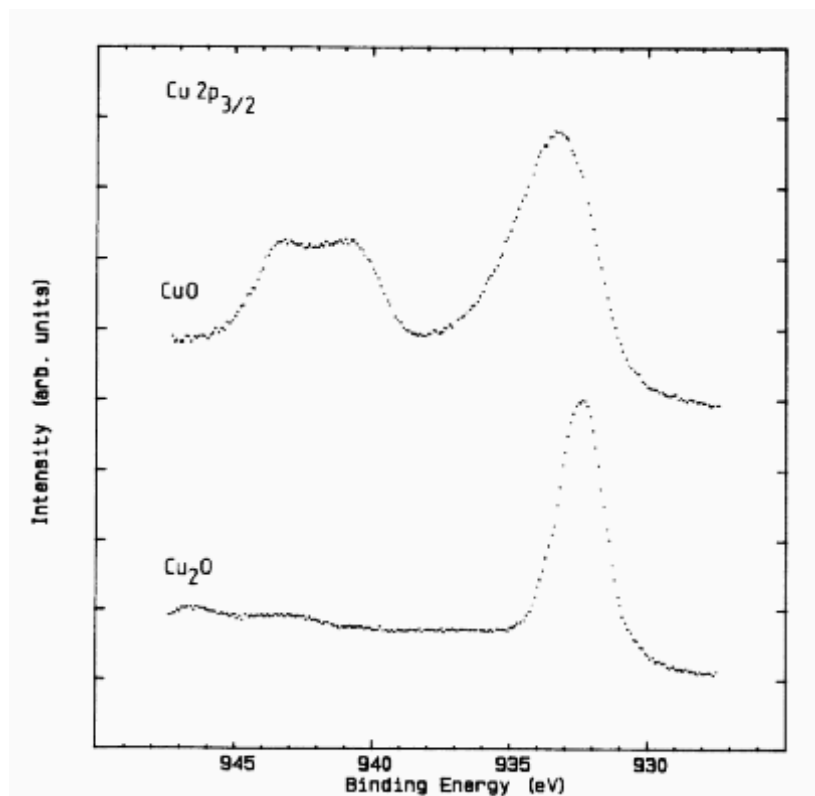

Fig. 1.2-1 $Cu2p_{3/2}$ spectra for Cu_2O (bottom) and CuO (top) normalized at peak height. The data are taken from Ref. [GTE88].

In order to illustrate characteristics of their XPS spectra, Fig. 1.2-1 presents the $Cu2p_{3/2}$ spectra of Cu_2O (bottom) and CuO (top) measured by using Al Kα radiation. In the spectrum of CuO a pronounced satellite is found at about 9 eV higher binding energy than the main peak whereas in the Cu_2O spectrum this satellite has little or no weight. Also, the main line in the CuO case is much broader than in the spectrum of Cu_2O. In general, concerning the copper features, the XPS spectra of compounds that have formally divalent copper in the ground state show similarities with the spectrum of CuO (existence of pronounced satellite peaks), and those of the compounds where copper is monovalent resemble the Cu_2O spectrum.

The existence of satellites in the spectra of CuO and of compounds where copper is divalent was generally explained in a molecular orbital description by a charge transfer

mechanism [LWH81, GTE88]. In these compounds, copper has a formal $3d^9$ configuration in the ground state. This corresponds to a $3d^9$ ground state with a small contribution from $3d^{10}\underline{L}$, where $\underline{L}$ represents a hole in the ligand [FGT2000]. Photoionization at the copper site can lead to two final states: In one of them, after the core hole creation, the Cu3d level is pulled down below the ligand level by the Coulomb core-hole attraction and one electron is transferred from the ligand into the Cu3d level. This corresponds to the main line for which the final configuration is thus given by $\underline{c}3d^{10}\underline{L}$. In the other possible final state, no charge transfer takes place after the photoionization and the system is left in a $\underline{c}3d^9$ configuration, which is assigned to the satellite line [LWH81]. Here $\underline{c}$ and $\underline{L}$ denote a hole in the core level c and ligand, respectively. For the spectrum shown in Fig. 1.2-1, for example, c represents the Cu $2p_{3/2}$ core level. Fig. 1.2-2 shows a sketch of the processes which lead to the final states corresponding to the main line and to the satellite for the Cu2p photoionization of a compound with a copper $3d^9$ configuration in the ground state.
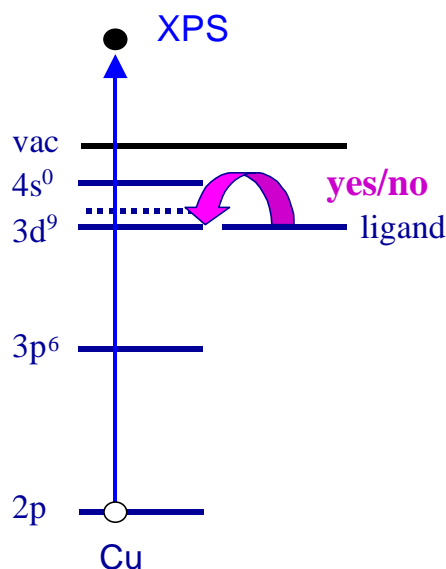

Fig. 1.2-2 Schematic description of the processes which lead to the final states corresponding to the main line (ligand-to-metal charge transfer) and to the satellite (no charge transfer) at the Cu2p photoionization of a compound with a copper $3d^9$ configuration in the ground state.

The absence of the satellites for Cu_2O is a consequence of the filled d shell. Hence no screening via charge transfer into the d states is possible [GTE88] and only one pronounced peak will appear in the spectrum.

The above mentioned considerations suggest that what is called 'satellite' could be regarded as 'main line' in the spectrum (is the state reached by direct ionization from a d^9 ground state) while what is called 'main line' could be considered as a shake-down

satellite. However, in this work the peak found at lower binding energy will be called 'main line' and that found at larger binding energy will be named 'satellite'.

The broadening of the main line in CuO compared to Cu$_2$O is attributed to the fact that the system can end up in several final states $\underline{c}d^{10}\underline{L}$, with different energies, depending on the energy of the valence hole $\underline{L}$ [KGJ2000].

Van der Laan et al. [LWH81] have analyzed the copper satellites taking as example the spectra of insulating copper dihalides (copper difluoride, copper dichloride and copper dibromide) in a model involving the ligand (L) and the metal orbitals. These are reference calculations and discussions related to this model can be also found in other studies [as for example Hüf83, DCG88, Hüf95, PMP2001]. In copper dihalides the copper is formally divalent, thus having one hole in the d shell, while the ligand shell is full. The Cu2p photoemission spectra of copper difluoride, copper dichloride and copper dibromide, taken from Ref. [LWH81] are presented in Fig. 1.2-3.
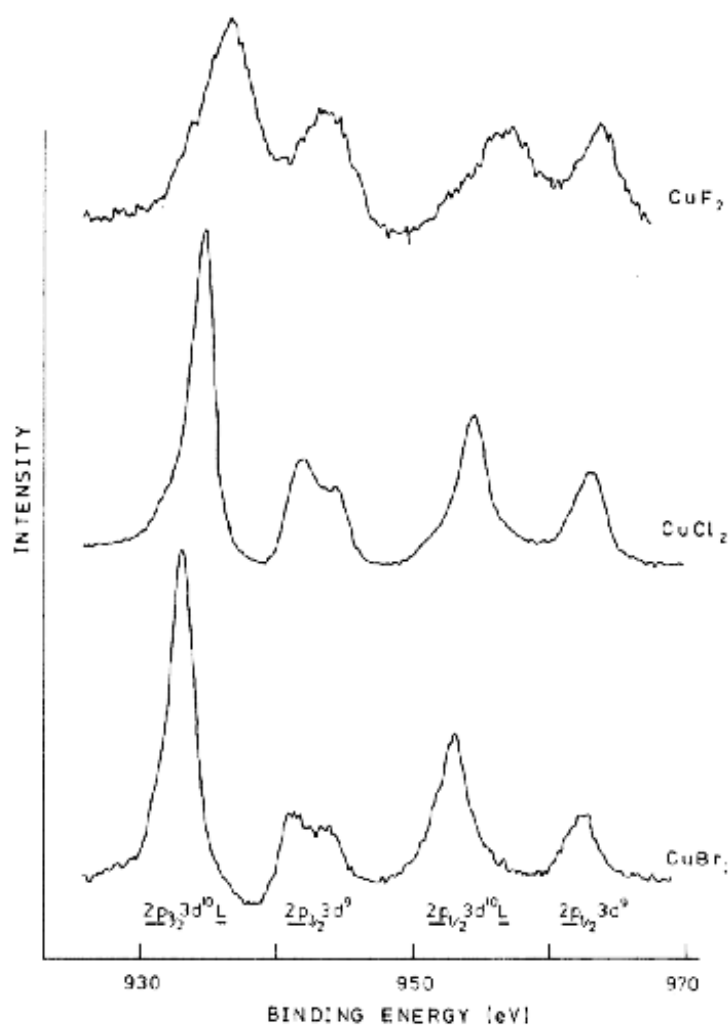

Fig. 1.2-3 Cu2p photoemission spectra for copper dihalides. The data are taken from Ref. [LWH81].

They show the main characteristics of the spectra for compounds where copper is in a nominally $3d^9$ configuration. Thus the main lines for the two split components are assigned to correspond to a $\underline{2p}_{1/2}3d^{10}\underline{L}$ and $\underline{2p}_{3/2}3d^{10}\underline{L}$ final configuration, and the satellites correspond to $\underline{2p}_{1/2}3d^9$ and $\underline{2p}_{3/2}3d^9$, respectively.

A comparison of the spectra for CuF_2, $CuCl_2$ and $CuBr_2$ shows that the main line (strongest line) has significantly different binding energies for the different dihalides while the satellite line has approximately the same position. This is also true for the spectra in the region of other inner levels, as for example 3p. Such a behavior can be explained by the final configuration corresponding to the main line, $\underline{c}3d^{10}\underline{L}$. Neglecting the interaction between the ligand hole and the electrons or holes on the copper ion, the energy of the main line can be expressed as

$$E_{main} = E\left(\underline{c}d^{10}\underline{L}\right) \cong E\left(\underline{c}d^{10}\right) + E\left(\underline{L}\right). \qquad \text{E 1.2-1}$$

The dependency of the main line energy on the ligand is explained by the fact that the highest occupied ligand shell is different for the investigated compounds (this is 2p for F^-, 3p for Cl^- and 4p for Br^-). Therefore the energies of the main core lines carry information about the valence ligand binding energy [LWH81].

The energy of the satellite line can be written as

$$E_{sat} = E\left(\underline{c}d^9\right). \qquad \text{E 1.2-2}$$

Thus, the energy of the satellite does not depend on the ligand to a first approximation.

For calculating the intensity ratio between satellite and main line, as basis for the calculations it was considered that the eigenstates in the initial state are a linear combination of $\psi\left(3d^9\right)$ and $\psi\left(3d^{10}\underline{L}\right)$. The energy difference between the two initial states in the valence band (charge transfer energy) is

$$\Delta = E\left(3d^{10}\underline{L}\right) - E\left(3d^9\right) \qquad \text{E 1.2-3}$$

and the mixing matrix element between these states is given by

$$T = \left\langle \psi\left(3d^9\right)\left|H\right|\psi\left(3d^{10}\underline{L}\right)\right\rangle. \qquad \text{E 1.2-4}$$

If the overlap is neglected the eigenvalues are calculated to first order as

$$E_{1,2} = E_0 + \frac{1}{2}\Delta \pm \frac{1}{2}\left(\Delta^2 + 4T^2\right)^{1/2}, \qquad \text{E 1.2-5}$$

where E_0 is the energy for $\Delta, T = 0$.

In the final state there is an additional hole in a core level of copper and therefore one needs to consider the Coulomb interaction between this hole and and the charges on the copper atom and on the ligand. To a first approximation, neglecting the Coulomb interaction between the copper core hole and ligand, and only accounting for the Coulomb interaction Q between the copper core hole and the d-configuration, the eigenvalues are:

$$E_{s,m} = E_0{}' + \frac{1}{2}\Delta \pm \frac{1}{2}\left[(\Delta - Q)^2 + 4T^2\right]^{1/2}.$$ E 1.2-6

Thus, the energy separation between satellite and main line is

$$W = E_s - E_m = \left[(\Delta - Q)^2 + 4T^2\right]^{1/2}.$$ E 1.2-7

With the above mentioned considerations, the intensity ratio of the satellite and main peak is calculated to be

$$\frac{I_s}{I_m} = \tan^2(\theta' - \theta),$$ E 1.2-8

where $\tan 2\theta = 2T/\Delta$ and $\tan 2\theta' = 2T/(\Delta - Q)$. Thus the intensities of the satellites contain information about the relative positions of the Cu3d and valence holes and the degree of hybridization [LWH81]. The orbital hybridization, determined by T, reflects the covalency degree in a certain copper compound. As remarked by Kawai et. al. in [KTI94], if Δ is small, the compound is covalent and if $|T|$ is large the compound is also covalent. Therefore, the intensity ratio between satellite and main line is small for covalent copper compounds and large for ionic ones [KTI94].

This kind of information can be deduced in principle from the satellite intensities of any of the core lines of Cu, even if the simplest case seems to be for Cu2p lines.

In the valence band of compounds containing divalent copper, the satellites have been ascribed to a $3d^8$ final state configuration while the main line to $3d^9\underline{L}+3d^{10}\underline{L}^2$. The $3d^8$ configuration for the satellites was proved by the resonant photoemission experiments [TBH82, GTE90, TCG91, QAA95, TBS2001]. The estimation of satellites intensities is difficult for the valence band partly due to the fact that the covalent mixing of $3d^8$ state with strong term splittings with the $3d^9\underline{L}$ state having small term splittings should be taken into account. The satellites have reduced intensity in the valence band compared to the inner core levels region and the matrix element connecting these states is considered to be significantly smaller than that corresponding to the core satellites case $T = \left\langle \underline{c}d^9 \left| H \right| \underline{c}d^{10}\underline{L} \right\rangle \approx \left\langle 3d^9 \left| H \right| 3d^{10}\underline{L} \right\rangle$.

Concerning the photoemission spectra, a complettly different situation than that described for divalent copper compounds is met for Zn^{2+} complexes. In divalent zinc compounds the 3d shell is filled and no satellite structures were observed in the region of $Zn2p_{1/2,3/2}$ core levels [RWG71, MuH79].