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by

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ABSTRACT

Partial photoionisation cross sections of valence bands and outer atomic levels in solids show anomalies at the thresholds of core electron excitation. For the rare earths and the transition metals and their compounds these coupling phenomena are dramatic resonances. The quantitative investigation of these effects provides insight into many-body effects in solids and has useful application for the investigation of the valence state of atoms in solids.

1. INTRODUCTION

I wish to approach my topic from an experimentalists point of view trying to use fundamental and simple pictures. In order to speak about shells in a solid one has to consider the individual atoms embedded into a solid state continuum. The outer electrons and also the unoccupied states above the Fermi level glue together the solid in the form of bands while the inner electrons occupy virtually unchanged atomic shells.

As a result spectroscopists are widely used to interpret an absorption spectrum of a solid as shown in Fig. 1, namely as a superposition of the contribution from different subshells. While in absorption spectra the "tails" of the partial subshell cross sections are decomposed by a "reasonable" extrapolation, photoemission spectroscopy allows to measure these cross sections individually.

Such a picture is suggestively supported by the independent particle model of the periodic table of elements and the Hartree-Fock model of calculating many electron systems. In this model all electrons but the one which is excited directly are kept rigid and thus unaffected by the excitation. Also the X-ray absorption spectra appear to support such a model at first sight.

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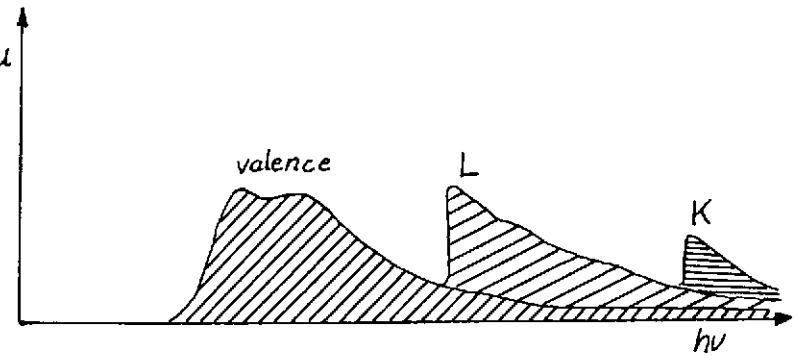


Fig. 1. Schematic absorption spectrum

The coupling of electrons of different shells and of electrons within the same shell must, however, clearly influence the excitation spectra of solids. This is quite obvious from the fact that during the excitation process all other electrons in the system experience the force due to a sudden change in the electrostatic potential. The electrons react and thus try to screen the field. In doing so the system is subject to its quantum mechanical boundary conditions.

These coupling effects are difficult to treat theoretically since they involve complex series expansions of the many-body interactions which can be treated only approximately. Nevertheless a tremendous progress has been made in the theory of these processes[1-3].

The VUV (vacuum ultraviolet) is the spectral regime where these coupling phenomena play an essential role. Even from a phenomenological point of view these effects are visible in a large number of absorption spectra of different materials. I want to mention the Fano profiles of discrete absorption lines superimposed into the continua in the spectra of solid and atomic rare gases[4], the 100 eV resonance peak in solid and atomic Xe[5], probably the best known test example of many-body theories, the rare earths at the 4d excitation threshold[6] and the transition metals at the 3p threshold[7] among others. In all absorption spectra, however, these coupling phenomena are detected only through a comparison between theory and experiment. In other words these effects are not a new experimental phenomenon. They are recognized only in the difference between experiment and a good one electron calculation. As long as such discrepancies are large compared to experimental uncertainities and computational errors it is not difficult to find these effects. Smaller coupling phenomena may, however, be hidden in both error bars.

There is, however, at least one class of coupling phenomena, namely the intershell coupling, which can be recognized by experimental techniques alone without reference to a theoretical calculation. The technique is to measure the partial cross section for the excitation of an outer atomic level (or a valence band in a solid) over a large energy range continuously. When the photon energy passes through the threshold of an inner shell excitation the coupling with that specific shell is borne out by structures which in a one electron picture would belong to the inner shell excitation only. One of the first cases of such an investigation was the increase of the partial photoionization cross sections for the 5s and 5p excitations in Xe above the threshold of 4d transitions by West et al.[8] in 1976.

The occurrence of satellites to the photoemission lines of core and valence spectra is another manifestation of a many-body coupling of the electrons in matter. Such satellites are frequently interpreted in terms of two- or more-electron excitations. Since this phenomenon is at least as important in XPS as in UPS we do not consider it to be characteristic for the VUV. There is, however, a phenomenon which was first observed by Guillot et al.[9] in 1977, namely a resonance of the 6 eV satellite in EDC's of Ni metal near the Ni 3p threshold. Also such satellite resonances are a manifestation of intershell coupling. They are, however, fairly difficult to interpret[10].

In 1978 Lenth et al.[11] observed huge enhancements of several features in the valence bands of rare earth compounds at the 4d threshold. These rare earth resonance phenomena are probably the most clear-cut examples of intershell coupling. They provide up to date the spectra with the richest details. The intershell coupling in rare earth metals and their compounds have been widely investigated since. Several examples will be given in this paper.

This paper cannot be a complete review of this field but it rather is referring to recent work done by the group at the FLIPPER monochromator at the DORIS storage ring in the HASYLAB laboratory. Especially two recently completed thesis papers have been centered on this topic namely the work of J. Barth[12] and F. Gerken[13].

Before I shall discuss some recent results I want to mention a few experimental problems and the approach with which we have tried to solve them.

2. EXPERIMENTAL PROBLEMS

In order to determine the partial cross section of a subshell correctly, the primary result, namely the variation of the intensity of peaks in an EDC as a function of $h\nu$, has to be corrected in several ways. In many of the early publications

not even the correction for the incoming photon intensity was made. This does not appear to be acceptable any longer since it leads to a lot of discrepancies in the results from different groups. The following corrections ought to be made[14]:

1. Normalization to the incoming photon intensity (typically measured by a calibrated Au diode), correction for straylight and higher orders,
2. correction for the mean free path of the photoelectrons,
3. correction for the escape and diffraction of the photoelectrons through the surface (which may be a problem when the surface is rough),
4. correction for the limited analyzer acceptance, which has to be transformed to the inside of the crystal by taking into account the surface refraction,
5. in connection with point 4 the anisotropic photoemission with respect to the electric vector of polarization given by the β-parameter ought to be considered but is usually not known, in addition the unknown effects due to the crystal asymmetry are neglected,
6. an additional problem is the background subtraction in the EDC's. While this needs a model for the shape of the peaks and for that of the scattering background, measurements taken in the "constant initial state mode" (CIS) contain a background contribution from the outset which is almost impossible to correct for,
7. finally a correction for the transmission of the electron analyzer as a function of the energy of the incoming photoelectrons must be made. This depends on the mode of operation (constant or varying pass energy modus).

In a paper by Barth et al.[14] all these corrections have been described in detail, the geometrical corrections are exemplified for the special geometry at the FLIPPER station at HASYLAB where a cylindrical mirror analyzer (CMA) is used. An example of the importance of these corrections will be shown below in Fig. 6 and Fig.7.

3. RARE EARTHS

In his thesis Gerken[13] has measured the spectra and the resonance effects for all accessible rare earth metals. Part of this work is published[15] and more will be published[16] soon. Also the earlier literature is cited there. Rare earths and their compounds are now intensively investigated with synchrotron radiation and XPS by many different groups (see also other contributions to this conference).

Figure 2 shows an EDC of Ce. The dashes indicate how the contributions from the different Ce states are separated. The background of scattered electrons was determined by a Monte-Carlo scattering simulation. We do not want to address here the recently heavily discussed question whether or not both peaks (E_B = -0.5 eV and E_B = -2 eV) are originating from the Ce 4f levels.

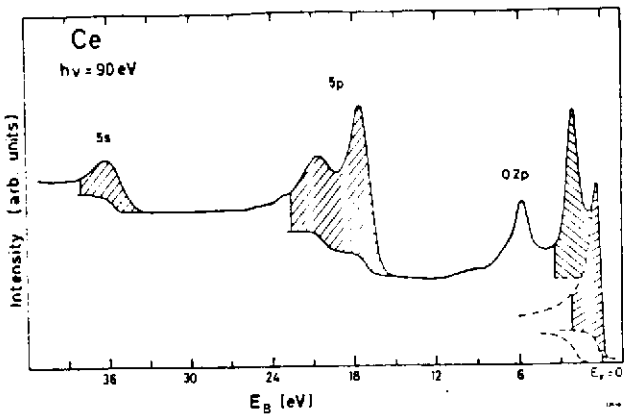
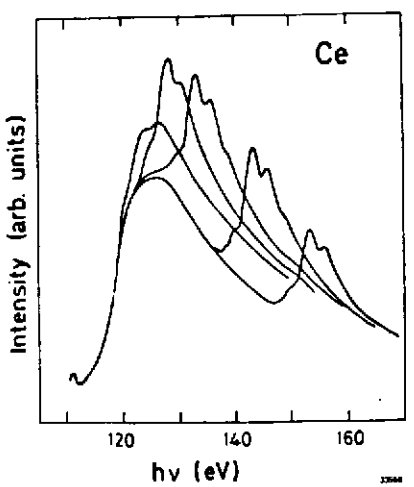


Fig. 2. Background subtraction for the curves Fig. 4 (from Ref. 13)



The direct 4d emission is difficult to obtain in this way since at threshold it is superimposed on the background of all scattered electrons on the far left side outside the limits of Fig. 2. The background is varying there considerably. Fig. 3 shows how these contributions are obtained from constant final state (CFS) spectra. Another method to obtain the 4d cross section is to monitor the 4d5pV-Auger intensity which is proportional to the real 4d holes created.

Fig. 3. Series of CFS-spectra, normalized to enable appropriate background subtraction. The final state parameter was set to kinetic energies 10 eV, 15 eV, 20 eV, 30 eV and 40 eV from left to right (from Ref. 13)

The sum of all these decay channels should give the absorption coefficient, which is proportional to the spectral dependence of the total photoelectric yield according to yield spectroscopy. Fig. 4 gives such a comparison. It shows the relative contributions of the different channels to the total cross section. With respect to the relative intensities the partial cross sections are in good agreement with a

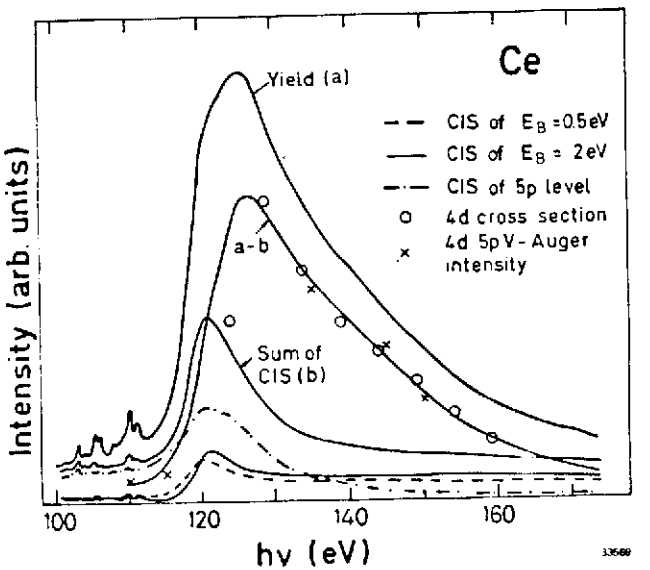


Fig. 4. Partial ionization cross sections for the different decay channels of the $4d^9 4f^2$ resonance.

theory by Zangwill and Soven[17]. The individual dependence on photon energy is, however, quite different.

A first analysis of this type was made by Hecht and Lindau[18] for Ba. Gerken[13] has performed the same analysis also for Pr, Nd, Eu and Gd.

Figure 5 shows the multiplet of the $4f^{11}$ final state configuration of Tm in an EDC. The line structure is well understood. Near the 4d threshold at 170 eV the individual lines undergo complicated fluctuations. The interpretation, as in all the rare earth spectra is that an intermediate $4d^9 4f^{13}$ state decays into the $4d^{10} 4f^{11}$ state through intershell interaction.

The CIS spectra in Fig. 6 show the dependence of the cross section on h for a few of the lines. The threefold structure in the cross section is due to the multiplet splitting of the $4f^{13}$ configuration. The differences for the peaks a, b, c are not yet understood. They need a detailed theoretical treatment as that described by Combet Farnoux[19] taking into account the actual states involved. Note that an uncorrected spectrum as that of Egelhoff et al.[20] can give (apart from the inferior energy resolution) quite distorted line shapes.

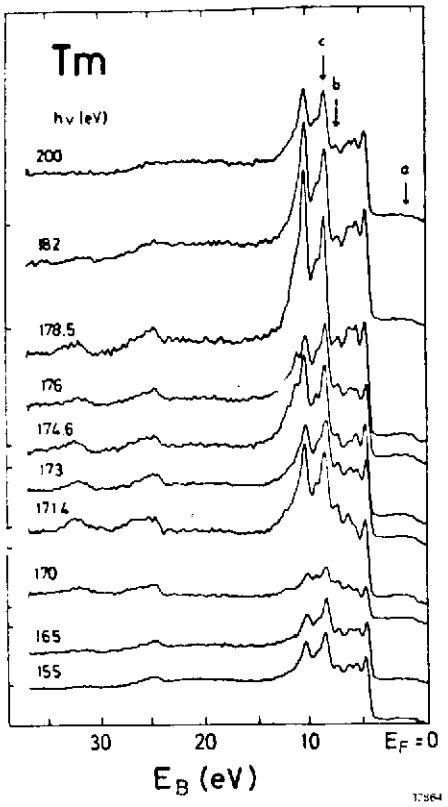


Fig. 5. Series of EDC's in the region of the 4d → 4f transitions. For a, b, c see Fig. 6 (from Ref. 13).

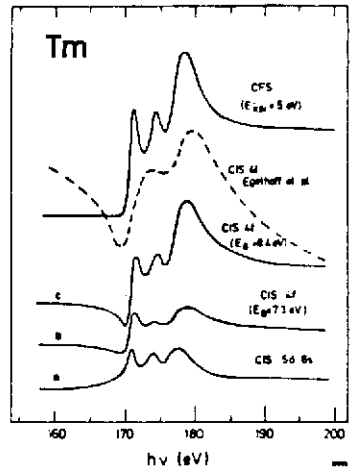


Fig. 6. CIS spectra for the structures a, b, c in Fig. 5 (from Ref. 13 and Ref. 20).

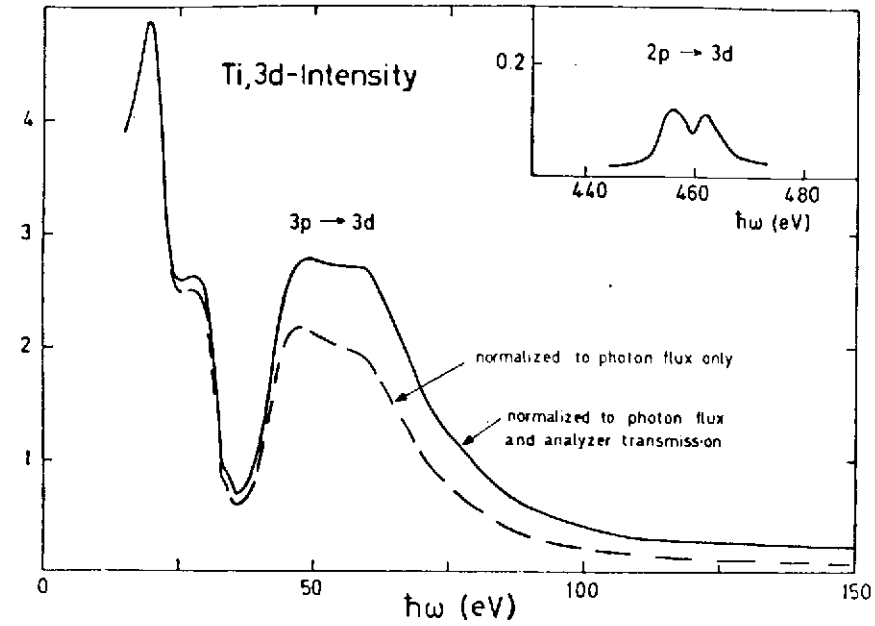


Fig. 7. 3d-intensity and partial cross section without the mean free path correction (from Ref. 12).

4. TRANSITION METALS

Figure 7 shows the partial 3d cross section for Ti over a large energy range as obtained by Barth[12]. Normalization to the photon flux when measuring over such a wide energy range is a necessity. But in addition, the analyzer transmission gives a considerable correction as shown. In this case the mean free path dependence on λ is not known, therefore the latter correction could not be made. It is interesting to note that the intershell coupling is not confined to shells with the same principal quantum number as in the rare earths 4d → 4f and here 3p → 3d. Also deeper shells are coupled as here 2p → 3d.

Figure 8 shows the 3d-spectra of the whole series[12] Ca to Cr. The onset of large structures is observed near the 3p threshold. The fact that such a strong interaction between the shells occurs already in Ca is due to an intermediate $3p^5 3d^1$ resonance state. Most remarkable are the double humps above threshold with a systematic increase of the second maximum over the first in the series. The corrections discussed

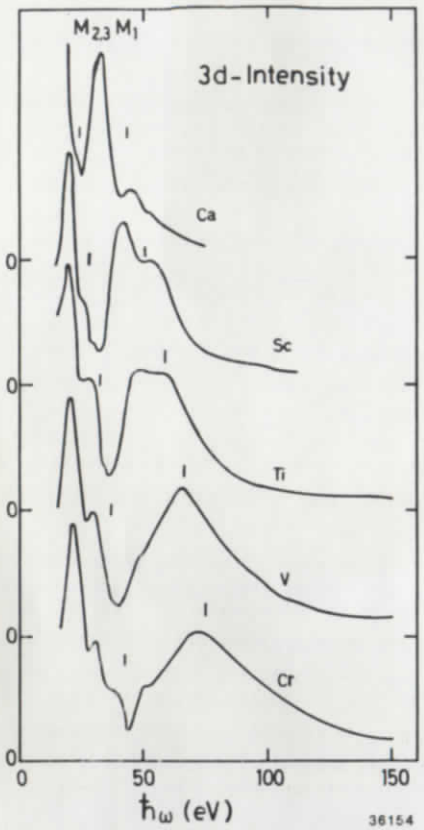


Fig. 8. 3d-partial cross sections (from Ref. 12).

5. TRANSITION METAL COMPOUNDS

In the study of atoms with open outer shells intershell interaction has shown its phenomenologically most prominent effects. The number of vacancies in the f or d shell has a large effect on the intemediate resonance state and thus on the signature seen in the cross section. This has been used for the study of valence fluctuations in rare earths, where the 4f occupancy changes, and in the change of 4f and d occupancy when rare earth and transition element compounds form. For transition metal compounds Ishii and his group (see subsequent paper and references cited therein) has done pioneering work. In some compounds of transition metals a hybridization of ligand electrons and the d states occurs. The theoretical aspects of resonances in-

volving such interatomic hybridization was studied by Davis[24]. We have investigated for this purpose[25] the series of Ni halides. While the systematic trends predicted by Davis are clearly showing up, I do not wish to discuss this aspect here in detail. The close connection with atomic spectroscopy in the gas phase is demonstrated here.

Figure 9 shows a series of EDC's of $NiBr_2$ at different photon energies in the vicinity of the Ni 3p threshold. For comparison we use a recently measured spectrum of Ni vapour by Schmidt et al.[26]. These authors have made a thorough investigation of the intershell coupling phenomenon with Ni vapour. Their spectrum consists of a d^7 and a d^8 configuration. They observe a two-humped resonance curve for the d^7 states while the d^8 states show a single resonance peak. Our peak 4 shows also a two-humped resonance, thus supporting an assignment of a d^7 configuration to our peak 4. The fact that our peak 4 has a much stronger resonance than the other peaks is in accord with Davis's theory[24]. While such a behaviour was predicted for the more covalently bound compounds as $NiBr_2$, in the strongly heteropolar NiF_2 the resonance shifts to the less intensily bound d-states in agreement with theory.

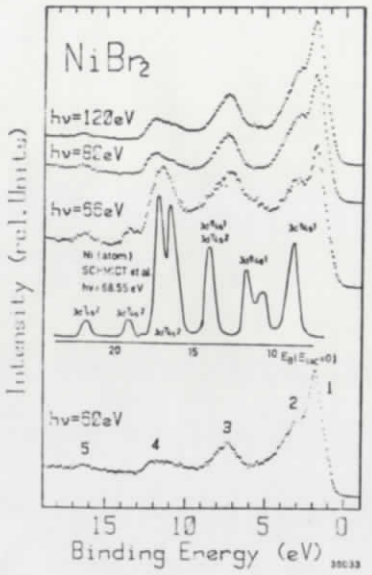


Fig. 9. $NiBr_2$ EDC's in the region of the 3p threshold. The gas spectrum is taken from Ref. 26.

6. CONCLUSION

Intershell coupling as observed in the partial photoemission cross sections of outer shell electrons has now been observed for a wide variety of substances. The most prominent effects occur for elements with incomplete shells and almost bound states.

A point has been reached where theorists attempt quantitative calculations rather than qualitative interpretations on simple models. This deserves, however difficult this may be, partial cross section measurements which are fully corrected for the instrumental response functions and the escape process of the photoelectrons.

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