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ANGLE RESOLVED PHOTOEMISSION FROM CLEAN SURFACES

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Résumé. — Pendant longtemps les méthodes optiques ont été les seules employées pour obtenir des informations sur la structure de bandes.

La photoémission angulaire qui est une amélioration d'une vieille technique est en train de devenir l'outil le plus puissant pour l'étude des niveaux électroniques.

Nous ne parlerons ici que des états de volume. Des exemples sont donnés pour trois cas types :

1) Les matériaux lamellaires pour lesquels il est possible d'obtenir la dispersion des bandes d'énergie d'une manière simple à cause de la faible dispersion le long de k_z .

2) Les semiconducteurs à trois dimensions tels que PbS et PbSe pour lesquels un modèle de densité d'états à une dimension permet d'expliquer les résultats expérimentaux et d'obtenir la dispersion le long de directions de haute symétrie.

3) Les métaux (Cu et Ni) : les résultats du cuivre, plus simple à cause de sa bande d complètement pleine, sont comparés à des calculs employant le formalisme de la diffraction d'électrons lents (DEL). Le problème des effets de corrélations est discuté brièvement. Enfin dans le dernier paragraphe nous rapportons la première observation d'un effet de résonance en photoémission.

Abstract. — For a long time the informations about the band structure of solids were obtained only by optical measurements. Angle resolved photoelectron spectroscopy (ARPES) which is a sophisticated refinement of an old technique has become a very powerful tool to get informations on the electronic levels.

We limit our discussion to volume states. Examples are given for three cases :

1) Layers materials for which it is possible to map the bands in a very simple way due to the flatness of the bands along k_z .

2) Three dimensional semiconductors as PbS and PbSe. For these an one dimensional density of states model explains very well the experimental data and allows also to obtain the dispersion along high symmetry lines.

3) Metals as Cu and Ni : in this case comparison is done with calculations using the L.E.E.D. formalism. The problem of correlation effects is shortly discussed. Finally a strong resonance effect observed for the first time in photoémission will be reported.

1. Introduction. — The aim of this talk is to present an overview of the possibilities of the angle resolved photoemission technique for the study of the electronic levels of solids.

I will not discuss at all the case of surfaces states or adsorbates : this part will be covered by N. Smith. Also for the volume states I will limit myself to energy distribution experiments and leave the constant final (CFS) and initial (CIS) energy spectra to G. Lapeyre, who will discuss also the polarization dependent photoemission.

Since the Hamburg Conference the activity in the area of angular resolved photoemission spectroscopy (ARPES) has been growing up very fast and it is impossible to cover all the field. I have been forced to choose few experiments and I apologize in advance for that. The principle of (ARPES) is quite simple ; let denote by θ the polar angle (angle between the analyzer and the normal to the surface) and by φ the

azimuthal angle (see Fig. 1) and collect only the electrons emitted in a small solid angle. In that case we measure not only the energy of the photoelectrons but also their momentum $\mathbf{K}$. The problem is to relate $\mathbf{K}$ to the wave vector of the electron in the solid $\mathbf{k}$. We will suppose that there is conservation of the component parallel to the surface [1]

$$\mathbf{K}_{\parallel} = \mathbf{k}_{\parallel} + \mathbf{G}_{\parallel} \quad (1)$$

where $\mathbf{G}_{\parallel}$ is the parallel component of any reciprocal lattice vector $\mathbf{G}$.

If E_c is the kinetic energy of the photoelectron

$$k_{\parallel} = \left[\frac{2 m E_c}{\hbar^2} \right]^{1/2} \sin \theta \quad (2)$$

we have to notice that $k_z = k_{\perp}$, the component of $\mathbf{k}$ perpendicular to the surface does not appear in the equation above and it is indeterminate : [2] this is the

FIG. 1. — Angles used in ARPES experiments; α is the angle between the photon beam and the normal to the surface.

main difficulty. So the first attempt was to study special cases :

— Layer compounds where the dispersion along $k_{\perp}$ is small in first approximation.

— Normal emission : by collecting only electrons emitted at the normal ($\theta = 0$, $k_{\parallel} = 0$) we can obtain the dispersion along $k_{\perp}$ by varying the photon energy $\hbar\omega$.

In section 3, I discuss the case of layers compounds. Section 4 is devoted to three dimensional semiconductors and we will show that the dream of determining the three dimensional band structure of a solid *directly* from experiment can be reached...

In section 5 we will review Cu and Ni which are quite interesting due to the difference in their d band and we will show that a sophisticated calculation using the L.E.E.D. formalism gives a remarkable agreement with experiment. Finally we will report on a strong resonance effect observed on nickel (100).

2. Experimental set-up. — Some of the experiments that I will discuss now were performed at the Orsay (ACO) storage ring : so I will describe shortly the system that we use there. It is quite similar to most of the photoemission set-up excepted that we have the chance to replace the He discharge lamp by the light emitted by the storage ring.

The following configuration (Fig. 2) is used : 5 mrad. of the light emitted by the storage ring are focused at the entrance slit of the monochromator by a toroidal mirror. The size of the point source S ($\varnothing = 1$ mm) is reduced by a factor 3. The monochromator (Jobin-Yvon LHT 30) is based on a simple [3] rotation of a toroidal holographic grating and gives a resolution

FIG. 2. — Experimental set up ; S is the point source in the storage ring.

FIG. 3. — Experimental chamber ; notice the level 1 where the surface can be characterized by Auger and L.E.E.D. and the level 2 where the analyzer can be rotated in the horizontal plane.

of the order of $1 \text{ \AA}$. At the exit the photon beam is focused to a size $< 0.5 \times 0.7 \text{ mm}^2$. The experimental chamber is represented on figure 3. At the first level the sample can be cleaved or ion bombarded and characterized by L.E.E.D. and Auger spectroscopies. At the second the energy analyzer, which is a 127° cylindrical type, is rotated around the sample. The acceptance angle is $1^\circ \times 2^\circ$ and it was operated at an energy resolution varying between 100 and 300 meV.

3. Layers compounds. — We look at shortly the properties of layer compounds which have made them attractive for angle-resolved photoemission experiments. As an example we have chosen GaSe which has been studied by different groups [4], [5], [6], [7] but I would like to mention the pioneering work of Smith and Traum on TaS_2 and TaSe_2 [8].

GaSe is a layered compound with a hexagonal structure; it consists of thin tightly bound layers. Each of these has four close-packed mono-atomic sheets (Se-Ga-Ga-Se).

The crystal structure is shown on figure 4. The stacking sequence of the sandwiches gives rise to a lot of crystal modifications (polytypes).

FIG. 4. — Crystal structure of GaSe (β).

The interaction between adjacent layers is of the Van Der Waals type.

The Brillouin zone (Fig. 5) is hexagonal and the important symmetry directions are ΓA , ΓM and ΓK .

FIG. 5. — Three (a) and two (b) dimensional Brillouin zone of GaSe.

In first approximation we suppose that the electrons are confined in the sandwiches which means that the dispersion along ΓA (perpendicularly to the plane of the layers) is small.

We suppose that the component of the wave vector parallel to the surfaces $k_{\parallel}$, is conserved during the emission process : in this case the relation between the kinetic energy E_c of the electron, the polar angle θ and $k_{\parallel}$ is given by equation (2).

If E_{val} is the energy of the initial state

$$E_{val} = E_c - \hbar\omega + W \quad (3)$$

where W is the energy difference between the vacuum level and the top of the valence band.

By combining (3) and (2)

$$E_{val} = \left[\frac{\hbar^2}{2m} \sin^2 \theta \right] k_{\parallel}^2 - (\hbar\omega - W) \quad (4)$$

we have two possibilities to obtain $E_{val}(\mathbf{k}_{\parallel})$:

- choose one $\hbar\omega$ and vary θ ,
- vary $\hbar\omega$ for a fixed θ .

We will consider the first approach where the final state is the same for any θ . The figure 6 shows the photoelectron energy spectra along the azimuth $\Gamma M \Gamma$ and $\Gamma K M \Gamma$ obtained for a photon energy $\hbar\omega = 27$ eV. The background due to the secondary electrons has been subtracted for clarity but has no influence on the structures.

FIG. 6. — Energy distribution curves of the photoelectrons in function of the polar angle, obtained at $\hbar\omega = 27$ eV along $\Gamma K M \Gamma$ and $\Gamma M \Gamma$ azimuths. A, B, C and D correspond to the groups of bands discussed in the text.

The valence band of GaSe has five groups of bands that we label (from the top of the valence band) A, B, C, D and E corresponding to two different bonds Ga-Ga and Ga-Se (if we neglect the weak Van der Waals interaction between layers). The gallium and selenium 4s and 4p atomic like orbitals are involved in these bands.

— The group A which corresponds to the uppermost valence band has a bonding character between the Ga atoms and a pronounced p_z like charge [9] is found around the Se atoms. This has been confirmed recently by polarization dependent photoemission experiments [10] showing that the peak corresponding to A disappears for s-polarized light.

— B is due to p_x, p_y orbitals in the Ga-Se bond (mostly covalent).

— The next two structures C and D correspond mainly to $s(\text{Ga})$ electrons. These states hybridize by adding p_z character and form a pair of bonding (D) and antibonding (C) bands of the Ga-Ga bond.

— E takes its origin from the 4s levels of Se. At low photon energy ($\hbar\omega < 50$ eV) we have not been able to observe this band which is seen by X. P. S. [11] and also at $\hbar\omega = 85$ eV [12].

We ignore the change in intensity of the different peaks and we follow the change in the positions when θ varies between 0 and 75° . The results are given in figure 7a for the $\Gamma M \Gamma$ azimuth and 7b for the $\Gamma K M K$. As seen by looking at the two dimensional Brillouin zone (Fig. 5) for a value of θ larger than 25° we move in the second zone. We expect to have a mirror symmetry about the M point and this is exactly verified. The figure 7c represents the bands in the reduced zone scheme : the dashed part (Fig. 8)

FIG. 7. — a) Experimental band structure obtained at $\hbar\omega = 27$ eV along the $\Gamma M \Gamma$ azimuth. Notice the mirror symmetry around M. b) Experimental band structure obtained at $\hbar\omega = 27$ eV along the $\Gamma K M K$ azimuth. c) Experimental band structure in the reduced zone scheme.

FIG. 8. — Comparison of the Schlüter's pseudopotential calculation (dashed part), shifted by 1.2 eV and the experimentally determined energy bands.//////, theoretical band structure shifted by 1.2 eV, — experimental band structure.

corresponds to the pseudopotential band structure of Schlüter [13] *et al.* There is an overall agreement if we shift the calculation by about 1 eV. There are some discrepancies concerning the bandwidth of the group B.

We have performed measurements also at $\hbar\omega = 33, 41$ and 45 eV and found that the dispersion of the bands is almost independent of the final state [14].

Very similar results have been obtained by Larsen *et al.* [15] for InSe (see Fig. 11) by Grandke and Ley for GeS [16].

Normal Emission :

It is easy [6, 17] to test the assumption that in the layer materials the bands have a small dispersion along $k_\perp$. If we work at the normal ($\theta = 0$ and $k_\parallel = 0$) and we suppose free electron like conduction bands

$$\frac{\hbar^2 k_\perp^2}{2m} = E_c + W_0 \quad (5)$$

where W_0 is the inner potential.

Then by measuring the photoemission distribution curves at $\theta = 0$ for various $\hbar\omega$ we obtain the dispersion along $k_\perp(\Gamma A)$. This has been done [16] for photon energies between 21 and 50 eV (Fig. 9). Using the equation (4), choosing arbitrarily the origin of W_0 and projecting the results in the first Brillouin zone we have obtained the dispersion along ΓA (Fig. 10a). We see that the bands B and D have almost no dispersion (≤ 300 meV). The experimental points of bands A and C show a strong variation in energy along ΓA . Since from the theoretical calculation [13] we expect two bands which are degenerate at Γ , contributing to each of these peaks, we take the energy variation of the experimental points as a strong evidence of dispersion although the points do not seem to align along distinct bands. Such a behaviour is expected for peak A from Schlüter's calculation of the electron charge density. He has found a pronounced p_z charge around the Se atoms extending towards the neighbouring layers ; then we expect a three dimensional character. The comparison with the Schlüter's calculation along ΓA

FIG. 9. — Energy distribution curves of the photoelectrons taken at $\theta = 0$ for various photon energy $\hbar\omega$ between 21 and 45 eV.

FIG. 10. — a) Energy dispersion of the bands in the direction ΓA . b) Band structure calculated by M. Schlüter [13].

is in a very good agreement. However we have to notice that the hypothesis of free electron-like conduction band is perhaps not quite correct for a layer compound.

The discussion until now has been limited to the positions of the peaks in the photoemission spectra. In fact there is more physics in the peak intensities but the interpretation is more complicated and as shown by Liebsch [18] needs calculations based on a L.E.E.D. type formalism. We should expect a large development of this field very soon.

FIG. 11. — Two-dimensional band structure for InSe along the $\Gamma M \Gamma$ direction. Open circles represent data for $\hbar\omega = 18$ eV; open squares represent data for $\hbar\omega = 24$ eV. Smooth curves have been drawn to pass near experimental points, as well as possessing mirror symmetry around the point M (from Ref. [15]).

4. Three-dimensional semiconductors. — As I said in the beginning of this talk in three dimensional systems we have a lack of information about the normal component $k_{\perp}$. That explains why very few experiments have been reported [19] and why the interpretation of the results is not very satisfying.

PbS.

Recently Granke, Ley and Cardona [20] have shown that the data on PbS (rocksalt structure) can be understood in terms of the one-dimensional density of states calculated along lines defined by $\mathbf{k}_{\parallel} = \text{constant}$ in reciprocal space. They suppose that transition matrix elements are not strongly dependent on the energy of the initial state. The angular resolved photocurrent with electron energy E created by photons of energy $\hbar\omega$ is :

$$I(E) \sim \iiint d^3\mathbf{k}_v \delta(E_v + E - \hbar\omega) \delta(\mathbf{k}_{\parallel v} - \mathbf{k}_{\parallel}) \quad (6)$$

where $\mathbf{k}_v$ is the crystal momentum of a valence band states, $\mathbf{k}_{\parallel v}$ the component of this momentum parallel to the surface, $\mathbf{k}_{\parallel}$ the corresponding component of the photoelectron momentum and E_v the energy (measured

with respect to the vacuum level) of the valence band state of momentum $\mathbf{k}_v$.

Two modes of measurement are possible. The one used here corresponds to keep θ constant. However, theoretically it is more convenient to treat the case in which $\mathbf{k}_\parallel$ is kept constant (varying θ while E is being swept). Since for a given θ and E , $k_\parallel$ is fixed only those valence electrons with $\mathbf{k}_{\parallel v} = \mathbf{k}_\parallel$ contribute to the photo current. According to [6] the ARPES spectrum represents the density of states of the one-dimensional sections of the valence bands-obtained by setting

$$I \sim \sum_{\text{val. band}} \left[\frac{dE_v}{dk_{\perp v}} (\mathbf{k}_{\parallel v}, \mathbf{k}_{\perp v}) \right]_{E_v = \hbar\omega - E_c}^{-1} \quad (7)$$

In view of the sharp peaks associated with the singularities in one-dimensional density of states, they estimated that the condition $\theta = \text{constant}$ (used in the experiments) did not significantly shift the peaks in an ARPES spectrum.

The figure 12 shows the Brillouin zone of a f.c.c. crystal. One dimensional densities of states were calculated along $k_{\parallel v} = \text{constant}$, as indicated by the vertical lines using the Empirical Pseudopotential Method and the coefficients given by Kohn [21] *et al.* (the spin-orbit interaction is neglected).

FIG. 12. — Extended zone scheme of the fcc-structure. The measurements were confined to irreducible wave vectors $\mathbf{k}_v$ lying within the square X-X-X- Γ . One dimensional densities of states were calculated along $\mathbf{k}_{\parallel v} = \text{constant}$, as indicated by the vertical lines. (Ref. [20].)

The energy dependence in $I(E)$, given by equation (7) as a function of $\mathbf{k}_{\parallel v}$, is plotted in figure 13a for the upper valence bands, mainly derived from the 3p levels of sulphur. Full lines correspond to critical points located at $k_{\perp v} = 0$ (i.e. along Γ - Δ -X), dashed lines to critical points at $k_{\perp v} = 2\pi/a$ (i.e. along X-Z-W-Z-X), and dotted lines to critical points at some intermediate value of $k_{\perp v}$.

The figure 13b shows the experimental peak positions versus the corresponding electron momentum component $\mathbf{k}_\parallel$ (obtained for $\hbar\omega = 21.2$ eV). The crosses stand for intense peaks while the open circles

FIG. 13. — a) Dependence of the energies of critical points in the one-dimensional density of states on $\mathbf{k}_{\parallel v}$. The solid lines refer to critical points at $k_{\perp v} = 0$, the dashed lines to critical points at $k_{\perp v} = 2\pi/a$ and the dotted lines to critical points at an intermediate value of $k_{\perp v}$. (From Ref. [20].) b) Experimental peak position versus electron momentum component $\mathbf{k}_\parallel$. The experimental points are connected by lines to give energy *vs.* momentum similar in shape to those of figure 13a.

refer to weak peaks or shoulders. It is possible to connect these discrete points by continuous lines very similar in shapes to those of figure 13a. Thereby we are able to assign every observed peak to a critical point in the one-dimensional density of initial states.

The agreement between theory and experiment is within what can be expected for the accuracy of any band structure calculation. Some minor disagreements are visible around $|\mathbf{k}_\parallel| = \pm 0.25 (\text{\AA})^{-1}$ where weak shoulders appear that do not correspond to any calculated critical point. The absence of about 30 % of the predicted peaks is attributed to the absence of appropriate final state.

PbSe.

We have also performed experiments on crystals of the same family : PbSe. We have chosen to work at $\hbar\omega = 35$ eV. At this photon energy we expect that the mean free path of the photoelectron is of the same order of magnitude that the interatomic distance which means that we avoid the direct transitions band structure regime [2]. The experimental configuration used is shown on figure 14. The figure 15 gives some of the photoemission spectra obtained at $\hbar\omega = 35$ eV for different θ . From these results it is possible to plot the peaks position *versus* $\mathbf{k}_\parallel$ (Fig. 16). The three first valence band (within 0 and - 5 eV) are p derived, the

FIG. 14. — Extended zone scheme of PbSe; in our experimental configuration $k_{||}$ is along [011] and $k_{\perp}$ along (100).

FIG. 15. — Angle resolved photoemission spectra at $\hbar\omega = 35$ eV for θ varying between -2° and 16° (but data have been taken each 3° until $\theta = 45^\circ$).

FIG. 16. — Experimental peak positions versus $k_{||}$. ■ stand for peaks, □ for shoulders. The points are connected by lines to give curves similar in shape to those of figure 17. a) and b) correspond to two possible solutions for the first s band (mostly 6s of Pb and 4s of Se).

last two mostly s. For the last one (4s of Se) the cross section is low in this photon energy range : that explains the larger error bar.

We have represented on figure 17 the energy dependence of the maxima in $I(E)$ given by equation (8) as a function of $k_{||}$. For that we have calculated the one-dimensional density of states along $k_{\perp}$ using the band

FIG. 17. — Variation of the maxima of the one-dimensional density of states given by equation (8) with $k_{||}$. The solid lines refer to maxima along $X K \Gamma$ ($k_{\perp} = 2\pi/a$), the dashed lines to maxima along $\Gamma K X \Gamma$ ($k_{\perp} = 0$), the dotted lines to maxima at intermediate value of $k_{\perp}$ (calculated with the band structure of Ref. [21]).

structure of Kohn *et al.* [21]. The solid lines refer to maxima along $XK\Gamma$ ($k_{\perp} = 2\pi/a$), the dashed lines to maxima along $\Gamma KX\Gamma$ ($k_{\perp} = 0$), the dotted lines to maxima at intermediate value of $k_{\perp}$. We have drawn similar lines between the experimental points. Excepted the structure at -1.2 eV, all the others take their origin along $\Gamma KX\Gamma$ ($k_{\perp} = 0$) and $XK\Gamma$ ($k_{\perp} = 2\pi/a$); a) and b) correspond to two possible solutions for the fourth valence band.

In fact it is easy to show [22] that for high symmetry directions, the lines of figure 17 are *just the band structure*. Following that we have represented on figure 18 the experimental band structure along ΓKX .

FIG. 18. — Band structure of PbSe. The solid lines are the bands calculated by Kohn *et al.* (Ref. [21]); ○ and ● the experimental points.

The full lines correspond to the calculation of Kohn *et al.* [21] : the experimental points ● come from $\Gamma KX\Gamma$ and ○ from $XK\Gamma$.

The agreement for the p derived bands is remarkable. As already shown by X.P.S. [23] measurements the positions of the calculated s derived bands are incorrect.

In table I we compare the experimental and calculated energies [21, 24, 25] of some critical points and of the spin-orbit splitting at Γ and X.

Finally we have performed photoemission experiments at the normal ($\theta = 0$ and $k_{\parallel} = 0$). In a direct

FIG. 19. — Photoemission spectra taken at normal emission ($\theta = 0$, $k_{\parallel} = 0$) for photon energy $\hbar\omega$ between 28 and 43 eV.

TABLE I

Energy position of the electronic levels of the valence band of PbSe (in eV)

Band	Sym.	Exp.	Theory				Exp.	Theory		
			α	β	γ			α	β	γ
5	Γ_8^-	- 2	- 1.9	- 2	- 2	X_7^-	- 3.3	- 3.9	- 3.15	- 3.13
4	Γ_8^-					X_6^-	- 3.75	- 4.25	- 3.50	- 3.55
3	Γ_6^-	- 2.6	- 2.5	- 2.55	- 2.6	X_6^-	- 4.85	- 6.4	- 4.85	- 4.9
2	Γ_6^+	- 7	- 5.2	- 5.7	- 6.1	X_6^+	a) - 8	- 6.85	- 5.7	- 6.7
1	Γ_6^+	- 12.7	- 14.9	- 16.4	- 14.4	X_6^+	b) - 7	- 13.3	- 16.2	- 13.6
Δ_{s-o}		0.6	0.6	0.55	0.6	Δ_{s-o}	0.45	0.35	0.35	0.42

α) From reference [24].

β) From reference [21].

γ) From reference [25].

Δ_{s-o} is the spin-orbit.

transitions model we should be able to map the bands along $\Gamma X \Gamma$; in fact as shown on figure 19, no dispersion is observed. This is coherent with the previous results showing that at these photon energies one observes the density of states.

5. Metals. — I have chosen to discuss only two metals : copper and nickel. The reason of this choice is that they have d bands and very similar electronic structure. However their photoemission spectra look quite different : the experimental peaks of copper are very sharp, compared to nickel. To explain this difference the following reasons have been given :

— Lifetime of the hole [26] ; copper has a very long lifetime for the hole created in the d band (low density of states near the Fermi level). This gives rise to photoemission spectra with well defined structure. On the contrary Ni has a very high density of states and a short hole lifetime. A hole created near the bottom of the d band will decay by Auger processes before it has the possibility to move on another atom. Pendry [26] has introduced a lifetime which is a strong function of $(E - E_f)$ and improved the agreement between theory and experiment.

— Correlations ; Friedel [27] has suggested an other mechanism. In the case of nickel, correlations between

electrons can give rise to a slightly random potential and k is no longer exactly a good quantum number. To study this effect Noguera *et al.* [27] (this conference) have used a crude model (Hubbard with one s band) and have shown that this effect should be maximum in the half of the d band. We have to notice that it is not easy to know the importance of this effect.

Cu.

It seems that copper is an ideal metal for photoemission : by ideal I mean that the agreement between numerous experiments and theory is remarkable. Different angular [26], [27] resolved photoemission calculations have been performed. All of them use the same formalism (the final state is the complex conjugate of the L.E.E.D. wave function of an electron coming from the direction of the detector, muffin-tin potentials...) ; the main difference is in the shape of the surface potential.

The results of Spanjard *et al.* [27] are shown on figure 20 for Cu (100) (dashed line) ; the full line corresponds to the experiment of Ilver and Nilson [28]. One can see that remarkable agreement is obtained for different azimuthal angles (not only for the positions of the peaks but also for the intensity). Similar results are observed on the face (111) (Fig. 21). An important

FIG. 20. — Theoretical (---) and experimental (—) photoemission spectra of Cu (100). (Ref. [27].)

FIG. 21. — Theoretical (---) and experimental (—) photoemission spectra of Cu (111). (Ref. [27].)

point is that, at $\hbar\omega = 16.8$ eV, nearly all the observed experimental peaks are due to direct transitions in which both $k_{\parallel}$ and $k_{\perp}$ are conserved.

Recently Wehmer *et al.* [29] have used angular resolved photoemission at the normal ($\theta = 0$, $k_{\parallel} = 0$) over a large energy range ($30 \leq \hbar\omega \leq 160$ eV) to map the bulk band structure (Fig. 22). The experimental peak positions are compared with the Burdick's band structure [30]. The experimental points are derived from the equation (5) by the following steps. From the measured peak positions, relative to the Fermi level, it is easy to calculate the final state energy. The magnitude of the final state wave vector is given by

$$|\mathbf{K}| = \left(\frac{2mE_f}{\hbar^2} \right)^{1/2}$$

FIG. 22. — Comparison of experimental peak position with Burdick's band structure of Cu for the direction (110). The bottom inset establishes a correspondence between photon energy and the part of the Brillouin sampled (Ref. [29]).

where the zero of the free electron scale is taken to the bottom of the free electron-like bands in Burdick's band structure. The relation $\mathbf{K}_{\perp} = \mathbf{k}_{\perp} + \mathbf{G}_{\perp}$ yield $\mathbf{k}$ in the first Brillouin zone and the corresponding values are plotted as bars in the figure. The inset at the bottom of the panel establishes a correspondence between $\hbar\omega$ and the part of the B.Z. sampled. The more interesting point is the pronounced s-p resonance at $\hbar\omega = 45$ eV for bulk transitions arising near $k = (-0.5, -0.5, 0)$ in the B.Z. It is quite clear that we obtain the dispersion of the s band. However we have to point out that above 70 eV, the mean free path of the photoelectron is quite short (~ 3 Å) and that should break the coherence of the wave (non-conservation of $k_{\perp}$). Above this energy we are in a X.P.S. regime as shown by Feibelman and Eastman and we should obtain the density of states along (110). Also this direct transitions model does not explain completely the results of Heimann *et al.* [31] obtained at lower photon energies ($\hbar\omega = 16.8$ and 21.2 eV).

Ni.

I would like to discuss now a resonance effect observed on one of the structures of the valence band of Ni. We have observed it in an angle resolved photoemission experiment but it should be visible in angle integrated experiments also [32].

X-ray (X.P.S.) and ultraviolet (U.P.S.) photoemission spectra [33, 34, 35] of a clean Ni (100) surface show a weak structure at approximately 6 eV below the Fermi level. The interpretation of this feature has been quite controversial. The X.P.S. core-level spectra (2s, 3s, 3p) have also a satellite structure at about the same energy, which has been attributed to a localized many body effect in the final state [36]. It has been suggested [34] that the X.P.S. valence-band feature might be analogous to this because of the strongly localized character of the d-bands in nickel.

However, in recent experiments with synchrotron radiation between 23 eV and 40 eV Smith *et al.* [35] have concluded that this weak structure is consistent with a simple band picture for an electronic transition originating from the s-p band, Δ_1 .

We have studied this structure experimentally in photoemission from Ni for photon energies $\hbar\omega$, ranging from 40 eV to 100 eV. We observe a strong resonance enhancement for $\hbar\omega$ in the neighbourhood of the 3p energy levels ($E_{p^{3/2}} = 66$ eV ; $E_{p^{1/2}} = 67.6$ eV). Off resonance the structure is still visible, both on the high- and low-energy side, but with rapidly falling intensity, especially on the low-energy side. The asymmetric line shape [37] is suggestive of resonant interaction between an excited quasi-discrete level ($3p^5 3d^{10} 4s$) and an ionized continuum ($3p^6 3d^8 4s$ plus emitted electron) : this is the model we chose to interpret our data.

The experiments, which are not discussed here in detail, were performed at the Orsay ACO storage ring. Throughout the experiment, outgoing electrons were collected normal to the nickel single crystal (100) surface. This was prepared by the usual methods : ion bombardment and annealing under ultra-high vacuum (less than 2×10^{-10} torr). The surface was monitored by low-energy electron diffraction and Auger spectroscopy and care was taken to avoid oxygen contamination, since the oxygen 2p orbitals give by themselves a peak at about 6 eV below the nickel Fermi level.

Experimental results are shown in figure 23 for twelve different incident photon energies, between $\hbar\omega = 63$ eV and $\hbar\omega = 83$ eV. For $\hbar\omega = 63$ eV the photoemission spectrum consists of two main features : a sharp peak structure A at about 1.5 eV below the Fermi level, due to the 3d bands of nickel, and the much weaker structure B at 6 eV below E_F . The structure B shows strong resonant behaviour as $\hbar\omega$ is tuned through the energy corresponding to the 3p-to-conduction-band transition (see $\hbar\omega = 67$ eV curve in figure 23). On the high-energy side of B, for $\hbar\omega \geq 69$ eV, a new peak appears : this is a well-characterized Auger transition and it is indicated by an arrow on figure 23.

The area under the structure B as a function of $\hbar\omega$, i.e. the line shape of the experimental resonance curve, is plotted in figure 24. It shows a marked asymmetry

FIG. 23. — Photoemission spectra of Ni (100) for photon energy $\hbar\omega$ between 63 and 81 eV. The peak A corresponds to the d bands; B (dashed area) is the structure located at 6 eV from the Fermi level. The arrows indicate the Auger transition.

which leads naturally to an interpretation of the phenomenon as a Fano resonance [37].

Considered from the atomic point of view, each Ni atom in the metallic ground state of nickel can be thought of as being, from the electronic point of view, in a coherent superposition of various configurations, but mainly of $(3d)^9(4s)$ and $(3d)^{10}$. It is the former which is responsible for the effect we find. The absorption process

FIG. 24. — Plots of the area of the B peak structure versus the photon energy in the vicinity of the 3p levels. The points are experimental. The full line corresponds to the values given by equations (9)-(12) with the following parameters $\Gamma = 2$ eV, $q = 2.5$ and $E_0 = 66$ eV.

produces a quasi-discrete state which, through a Coulomb (autoionizing) interaction V_E , is hybridized with a continuum

This Fano-type interaction, [37] with its characteristic asymmetric lineshape, has been suggested to be the physical origin of the structure observed in soft-X-ray absorption [38, 39] and in electron-loss spectra [40] for nickel metal. The Fano interaction yields a spectral line with its typical resonance-antiresonance features and described by the simple formula

$$I = \frac{(q + \varepsilon)^2}{1 + \varepsilon^2} \quad (8)$$

where

$$\varepsilon = \frac{(\hbar\omega - E_0)}{\Gamma} \quad (9)$$

$$\Gamma = \pi |V_E|^2 \quad (10)$$

is the spectral half-width of the autoionized state, and

$$q = \frac{(3p|r|3d)}{(3d|r|\varepsilon f)} \times \frac{1}{\pi V_E}. \quad (11)$$

In these formulae E_0 is the displaced energy for the transition r indicates dipole matrix elements and $|\varepsilon f\rangle$ is the f-partial wave of the unbound electron [40, 41].

We have fitted our experimental data to equation (9) and, as shown in figure 24, we find good agreement for $q = 2.5$, $\Gamma = 2.0$ eV and $E_0 = 66$ eV. Our value for q is considerably larger than those obtained from either energy loss spectra [40, 42, 43] ($q = 0.9$ and $q = 1.3$)

or theoretical calculations [40, 44] ($q = 1.8$). The values of Γ and E_0 are in excellent agreement with previous values [40, 44]. It should be emphasized that because of the experimental resolution and uncertainties, and the atomic model and simplifying assumptions [41], a fit better than the one obtained and quoted above can only be considered fortuitous. However, as shown in reference [32], the metallic character cannot be completely ignored in our interpretation.

It should be of considerable interest to study the photoelectron spectrum of atomic Ni in the same range of energies. A comparison with our present experiments would then yield information on the relative contributions of the one-electron band struc-

ture and of the electron-electron atomic-like correlations in metallic Ni.

6. Conclusion. — In my talk I have reviewed only energy distribution experiments : with the possibilities of source as synchrotron radiation (tunability, high flux, polarization, higher energy available...) it is easy to understand why this field is growing so fast.

The last parameter that we have to measure now is the spin of the photoelectron ; I bet that, at the next Vacuum Ultraviolet Radiation Physics Conference this will be done by many teams.

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