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3p-EXCITATIONS OF ATOMIC AND METALLIC Fe, Co, Ni AND Cu

by

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Abstract

The photoabsorption of atomic Fe, Co, Ni and Cu has been determined in the energy range from 45 eV to 90 eV. For Co, Fe and Ni there is a strong asymmetric resonance at the 3p-threshold which is attributed to $3p^6 3d^n \rightarrow 3p^5 3d^{n+1}$ transitions. These transitions are split by the interaction of the 3p hole with the partly filled 3d-shell and the 3p spin-orbit interaction and considerably modified by the interaction with the $3p^6 3d^n \rightarrow 3p^6 3d^{n-1} \epsilon f$ transitions. The two channels are strongly coupled via the "super Coster-Kronig" decay $3p^5 3d^{n+1} \rightarrow 3p^6 3d^{n-1} \epsilon f$. The dominant absorption band is conserved in the spectra of the metals whereas the rich atomic fine-structure at the 3p-threshold and approximately 10 eV above is washed out. The 3d-shell is filled in Cu and therefore the strong 3p - 3d resonance is missing in the spectra of atomic and metallic Cu.

I. Introduction

At the 3p-threshold the excitation spectra of the transition metals Fe, Co and Ni show strong asymmetric resonances (Sonntag *et al.* 1969, Wehenkel and Gauthé 1974, Dietz *et al.* 1974, Brown *et al.* 1971, Davis and Feldkamp 1976), whereas in Cu the corresponding resonance is missing (Haensel *et al.* 1968).

The width of the resonance by far exceeds the width of the empty 3d-band (McAlister *et al.* 1975). One-electron band models therefore fail to explain the spectra. The localized character of the 3p-hole and the partly localized character of the 3d-electrons favour an atomic approach, which has been proven very successful in the case of the core excitations of rare earths (Wolff *et al.* 1976). In order to test the validity of the atomic approach and to disentangle atomic and solid state effects we determined the 3p-absorption spectra of atomic Fe, Co, Ni and Cu.

2. Experiment

The atomic metals were maintained inside a new resistance heated tubular furnace mounted in front of a 2 m grazing incidence Rowland type spectrograph. To prevent alloying the metals were contained in an aluminium oxide tube. The temperatures ranged from 1150°C to 1980°C, which according to vapour pressure data corresponds to pressures between 0.5 and 2.5 Torr. The length of the vapour column was ~ 50 cm. Thin Al and carbon windows separated the vapour region from the high vacuum of the beam pipe and the spectrograph. Kr or Xe buffer gas prevented the metal atoms from reaching the windows. The windows and the buffer gas also served to suppress higher order background. The synchrotron radiation of the electron synchrotron DESY transmitted through the vapour column was focussed on the entrance slit of the spectrograph. The spectra were recorded on photographic plates. The spectrograph was calibrated by means of the known absorption lines of atomic rare gases (Codling and Madden 1965). The energy resolution at the 3p-threshold was 30 - 40 meV. From a series of plates obtained under different conditions (vapour pressure, exposure time, windows, buffer gas) the relative spectral dependence of the absorption coefficient has been established. The 3p-excitation spectra of atomic Fe, Co, Ni and

Cu presented in Fig. 1 have been normalized to those of the corresponding metals below the 3p-threshold and far above threshold. The energy positions of the maxima are listed in Table I.

3. Results and discussion

3.1 Atoms

Well resolved absorption lines show up at the 3p-threshold of Fe, Co whereas absorption lines could not be detected at the 3p-threshold of Ni. There are only broad lines (half width ~ 2 eV) at the 3p threshold of Cu.

Towards higher photon energies the absorption cross section of Fe, Co and Ni rises steeply, peaking ~ 5 eV above threshold. The steep rise is interrupted by well resolved shoulders. A series of sharp lines are superimposed on the decreasing continuum absorption in the energy range 60 eV - 64 eV for Fe, 67 eV - 70 eV for Co and 74 eV - 77 eV for Ni.

Underlying the 3p-absorption there is a strong background due to transitions from the 3d-shell. With the filling of the 3d-shell this background increases from Fe to Cu whereas the strength of the 3p-resonance band, which is proportional to the number of vacant 3d-states decreases (Starace 1972).

This explains why for Cu, which has a filled 3d-shell, the resonance band has disappeared. The $3p^6 3d^n 4s^2 \rightarrow 3p^5 3d^{n+1} 4s^2$ transitions dominate the spectra of Fe, Co and Ni at the 3p-threshold. In a first approach the relative energy positions and oscillator strengths of the transitions Fe $3p^6 3d^6 4s^2 5D_4 \rightarrow 3p^5 3d^7 4s^2$ ($J = 3, 4, 5$) have been calculated ab initio in intermediate coupling. These calculations neglect correlation. To correct for this the calculated Slater parameters have been scaled by 0.75. The results are given in Fig. 2. To facilitate comparison with the experimental spectrum the calculated spectrum was convoluted with a Lorentzian of 0.1 eV half-width. The assignment is given in Table I. The main oscillator strength is concentrated in the transitions $3p^6 3d^6 4s^2 5D_4 \rightarrow 3p^5 3d^7 ({}^4F) 4s^2 5D_{3,4}$, $5F_{3,5}$; $3p^5 3d^7 ({}^4P) 4s^2 5P_3$. This demonstrates that LS coupling is a good

approximation and that the $3d^6$ -electrons can be treated as spectators. Similar results have been reported by Combet Farnoux (Combet Farnoux 1974) for the Co $3p^6 3d^7 4F_{9/2} \rightarrow 3p^5 3d^8$ ($J = 7/2, 9/2, 11/2$) transitions. These results are shown in Fig. 3. The assignment based on these calculations is given in Table I. There are no corresponding calculations for the $3p^6 3d^8 4s^2 3F_4 \rightarrow 3p^5 3d^9 4s^2$ ($J = 3, 4, 5$) transitions of atomic Ni. But it is save to assume that the $3p^6 3d^8 4s^2 3F_4 \rightarrow 3p^5 3d^9 4s^2 3D_3$, $3F_{3,4}$ transitions comprise most of the oscillator strength and give rise to the structure at the 3p-threshold shown in Fig. 4.

In comparing experimental and theoretical results one has to take into account that at the elevated temperatures of our experiments states within one eV above the ground state are thermally populated. Especially for Ni this forms a serious problem because only 38 % of the atoms are in the $3d^8 4s^2 3F_4$ ground state. 18 % of the atoms are in the $3d^8 4s^2 3F_{2,3}$ states and 42 % in the $3d^9 4s 3D_{1-3}$ states (Moore 1952). The corresponding figures for Fe, Co and Cu approximately are: Fe $3d^6 4s^2 5D_4$ (ground state, 45 %), $3d^6 4s^2 5D_{0-3}$ (54 %), $3d^7 4s 5F_{1-5}$ (1 %); Co $3d^7 4s^2 4F_{9/2}$ (ground state, 49 %), $3d^7 4s^2 4F_{3/2-7/2}$ (41 %), $3d^8 4s 4F_{3/2-9/2}$ (10 %); Cu $3d^{10} 4s^2 S_{1/2}$ (ground state, 100 %). We have seen that for Fe, Co and Ni the most prominent structure above the 3p-threshold can be attributed to the 3p-3d transitions. For Cu the filled 3d-shell completely changes the situation. We ascribe the doublet at 73.15 eV and 75.40 eV shown in Fig. 5 to the transitions $3p^6 3d^{10} 4s^2 S_{1/2} \rightarrow 3p^5 3d^{10} 4s^2 2P_{1/2, 3/2}$. The separation of the peaks is determined by the spin orbit splitting of the 3p-hole. The assignment of the peaks at higher energies presented in Table I is based on the $Z + 1$ analogy model. For comparison the energy levels of Zn (Moore 1952) are included in Fig. 5.

The above results can be summarized in the following way: i) $3p^6 3d^n \rightarrow 3p^5 3d^{n+1}$ transitions dominate at the 3p-threshold of Fe, Co and Ni; ii) the multiplet splitting of the $3p^5 3d^{n+1}$ configuration is essential for explaining the width of the strong absorption band at threshold; iii) the energy positions and the oscillator strength of the calculated $3p^6 3d^n \rightarrow 3p^5 3d^{n+1}$ absorption lines correspond to the positions and strengths of the most prominent structures in the spectra.

Starting from this interpretation three questions arise:

- i) which mechanism broadens the strongest lines of the multiplets into the asymmetric absorption bands?
- ii) why do the lines at threshold persist?
- iii) which transitions are responsible for the sharp lines superimposed on the sloping background ~ 10 eV above threshold?

In analogy to the mechanism successfully applied to the rare-earths Dehmer et al. (1971), Dehmer and Starace (1972), and Starace (1972) proposed that the decay of the discrete excited states $3p^5 3d^{n+1} 4s^2$ into $3p^5 3d^n 4s^2$ ϵf is responsible for the broad asymmetric line shape. For Fe, Co and Ni no calculations based on this mechanism have been reported. An alternative mechanism has first been suggested by Dietz et al. (1974), and later on worked out in more detail by Davis and Feldkamp (1976). According to this mechanism the interference between the discrete $3p^6 3d^n 4s^2 \rightarrow 3p^5 3d^{n+1} 4s^2$ transitions and the continuum $3p^6 3d^n 4s^2 \rightarrow 3p^6 3d^{n-1} 4s^2 \epsilon f$ transitions mediated via the "super Coster-Kronig" decay $3p^5 3d^{n+1} 4s^2 \rightarrow 3p^6 3d^{n-1} 4s^2 \epsilon f$ leads to the broad asymmetric bands. By the quotation marks we want to point out that the super Coster-Kronig process is indistinguishable from the autoionization process, which leads to the same final state. Extending the formalism of Fano (1961) to the case of many discrete states interacting with many continua Davis and Feldkamp (1976

and 1977) calculated the $3p^6 3d^n \rightarrow 3p^5 3d^{n+1}$ absorption for metallic Cr (n=5), Mn (n=6), Fe (n=7), Co (n=8) and Ni (n=9). The free Fe, Co, Ni atoms have $3d^n 4s^2$ ground state configuration whereas the metallic configuration is closer to $3d^{n+1} 4s$ (Watson et al. 1976, Williams and Lang 1978). Therefore we compare our experimental spectrum for atom Z with the spectrum for atom Z-1 calculated by Davis and Feldkamp (1976). The small effect of the extra nuclear charge on the interaction between the 3p, 3d and ϵf electrons justifies this procedure. Figs. 2, 3 show that there is reasonable agreement between the experimental and theoretical results for Fe and Co. For Ni this procedure results in considerable discrepancies which can be attributed to the strong thermal population of the $3d^9 4s$ states. At the temperatures of our experiment only a small fraction of the Fe and the Co atoms are in the $3d^7 4s$ and $3d^8 4s$ states. Adding the theoretical spectra for Ni ($3p^6 3d^9$) and Co ($3p^6 3d^8$), weighted according to their thermal population results in the theoretical curve given in Fig. 4. The relative energy positions of the two spectra have been shifted. Fig. 4 shows that in this way fair agreement with the experimental spectrum can be achieved. Note that Davis and Feldkamp (1976) do not give absolute cross sections. In their numerical calculations they neglected the energy dependence of the half width Γ and the asymmetry parameter q . These quantities were calculated only once for each metal for an energy equal to some mean energy of the transition. This could explain why the well resolved lines at the low energy side of the dominant maximum of Fe and Co are absent in the theoretical spectra. Decay selection rules seem to drastically reduce the coupling of the discrete excited states, responsible for these lines, with the $3p^6 3d^{n-1} \epsilon f$ continua. For Mn this has been suggested by Connerade et al. (1976) and later on verified by Davis and Feldkamp (1978).

Transitions of the type $3p^6 3d^n 4s^2 \rightarrow 3p^5 3d^{n+1} 4s^2$ ms, md ($m > 3$) are probably responsible for the lines superimposed on the decaying continuum absorption ~ 10 eV above the 3p-threshold of Fe, Co and Ni. Double excitations may also contribute to the absorption in this energy range. Due to the large number of overlapping series converging to different ionization limits a detailed analysis of this region

forms a difficult task, which has not been tackled. In this context we only want to point out that the lines detected in this range are relatively sharp. This indicates that these states are not strongly coupled to the underlying continua. Because of the small overlap of the ms , md ($m > 3$) orbitals with the $3p$ and $3d$ orbitals $3p^5 3d^n 4s^2 \text{ ml} \rightarrow 3p^6 3d^{n-1} 4s^2$ *ef* autoionization processes are weak. This is consistent with the appearance of sharp lines. Besides autoionization the excited states can decay via the super Coster-Kronig transition $3p^5 3d^n 4s^2 \text{ ml} \rightarrow 3p^6 3d^{n-2} 4s^2 \text{ ml}$ *ef*. Assuming the influence of the bound excited ml electron to be small, i.e. neglecting relaxation, we are dealing with the same type of transitions which smear the $3p^6 3d^n 4s^2 \rightarrow 3p^5 3d^{n+1} 4s^2$ excitations into the broad absorption band at threshold. The existence of sharp $3p^6 3d^n 4s^2 \rightarrow 3p^5 3d^n 4s^2 \text{ ml}$ transitions requires the existence of the same type of decay selection rules already postulated for the decay of the $3p^5 3d^{n+1} 4s^2$ states. For example Davis and Feldkamp (1978) have shown that the "super Coster-Kronig" decay of the Mn $3p^5 3d^6 4s^2 \text{ } ^6D$ state is forbidden. From this we expect Fe $3p^6 3d^6 4s^2 \rightarrow 3p^5 3d^6 4s^2 \text{ (} ^6D \text{) ml}$ transitions to be sharp. Again we have made use of the fact that the interaction of the $3p, 3d$ and *ef* electrons is not much affected by adding an extra nuclear charge when going from Mn to Fe. Attributing part of the sharp lines under discussion to the simultaneous excitation of a $3p$ and one $3d$ or $4s$ electron leads to the same decay selection rules, because if we again neglect the relaxation of the outer electrons we always end up with the decay of the $3p^5 3d^n$ core. Consequently the appearance of the sharp lines superimposed on the continuum background is consistent with the "super Coster-Kronig" mechanism, proposed for the explanation of the lines and the broad absorption band at the $3p$ -threshold. The appearance of asymmetric Fano type profiles in this energy range would indicate that other decay channels, e.g. $3p^5 3d^n 4s^2 \text{ ml} \rightarrow 3p^5 3d^n 4s^2 \text{ } \epsilon \ell$ have to be taken into account, because the super Coster-Kronig decay $3p^5 3d^n 4s^2 \text{ ml} \rightarrow 3p^6 3d^{n-2} 4s^2 \text{ ml}$ *ef* does not give rise to interference with the one electron excitation continua.

For Fe, Co and Ni the lines ~ 10 eV above threshold do not show marked Fano type asymmetries, thus we conclude that interference effects are not important.

3.2 Metals

The spectra of the metals (Sonntag *et al.* 1969, Wehenkel and Gauthe 1973, Dietz *et al.* 1974, Brown *et al.* 1971, Davis and Feldkamp 1976) only show a strong asymmetric absorption band at the $3p$ -threshold. There are no structures corresponding to those showing up in the spectra of the free atoms (see Figs. 1,4). For Co a small peak preceding the main peak has been observed by Stearns *et al.* (1975) which has not been detected in other measurements. The small structure at the Ni $3p$ -threshold has been ascribed to the spin-orbit splitting of the $3p$ -level (Brown *et al.* 1971, Davis and Feldkamp 1976). Differences in the preparation of the samples are in part responsible for the discrepancies between the metal spectra reported by different authors. The overall shape and the width of the spectra of the metals agree with those of the free atoms. There is no marked shift of the threshold energy for Fe and Co whereas for metallic Ni the threshold is shifted by ~ 1 eV towards higher energies. The positions of the main maxima of the atomic and metallic spectra almost coincide. Part of the discrepancies between the spectra of the metals and those of the atoms are due to the different electronic configurations already mentioned above. This is obvious for Ni. There is no multiplet splitting at threshold because the $3d$ -shell is filled in the excited state. For Fe and Co this does not resolve all discrepancies because multiplet splitting exists for both configurations $3p^5 3d^n 4s^2$ (atom) and $3p^5 3d^{n+1} 4s$ (metal). For Cu metal the atomic lines are smeared out into a weak absorption band (see Fig. 5). The rise of the absorption is shifted towards higher energies by approximately 3 eV.

The calculations of Davis and Feldkamp (1976) very well reproduce the experimental spectrum of Ni metal. In contrast for Fe and Co metal there are similar discrepancies between theory and experiment as encountered in the comparison of the spectra of the metals with those of the atoms. The theory predicts marked structures which do not show up in the experimental curves. From our results we conclude that these discrepancies are due to solid state effects. Within the framework of a simple model one expects that upon solidification the 3p spectra are mainly affected by the following effects:

- i) broadening of the atomic d states into a band by the interaction of the d-electrons located at neighbouring atoms.
- ii) screening of the 3p-3d interaction resulting in a reduction of the multiplet-splitting.

For Fe and Co, starting from the atomic model discussed above, reasonable agreement between the experimental and theoretical results has been achieved in the following way:

- i) adding the d band width (McAlister *et al.* 1975) to the atomic width, thus increasing Γ to ~ 5 eV.
- ii) incorporating screening of the 3p-3d interaction by reducing the atomic multiplet splitting by a factor of ~ 0.7 . (This corresponds to a scaling of the calculated Slater parameters by ~ 0.5)
- iii) assuming that the asymmetry parameter q is not changed considerably upon solidification.

The characteristic features of the 3p spectra of the transition metals Fe, Co and Ni are clearly of atomic origin. The partly local partly itinerant character of the metal d-electrons manifests itself in the disappearance of the structures of the main absorption band upon formation of the solid. In the spectra of the metals, there is no obvious evidence for the importance of the mechanism proposed by Kotani and Toyozawa (1973) which is based on the s-d mixing interaction.

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Table 1. Energy positions of the peaks detected in the spectra of atomic Fe, Co, Ni, and Cu at the 3p-threshold. The numbers in brackets in column 3 give the relative uncertainty of the last digits. The assignment only refers to the contribution of the transition from the ground state of the atom.

Element	Peak	Energy (eV)	Absolute error (eV)	Assignment
Fe	1	51.423 (5)	.028	Fe $3p^6 3d^6 4s^2 5D_4 +$ $+ 3p^5 (2P) 3d^7 (4F) 4s^2 5F_5$
	2	51.688 (5)		$+ (2G) 4s^2 3H_5$
	3	51.915 (5)		$+ (2G) 4s^2 3H_4 + (4F) 4s^2 5F_3$
	4	52.100 (7)		$+ (2G) 4s^2 3G_5$
	5	53.65 (2)	.032	$(4P) 4s^2 5P_3$
	6	53.94 (2)		
	7	54.30 (2)		
	8	54.860 (15)		
	9	55.62 (3)		
	10	55.75 (3)		
	11	55.86 (3)	.040	$(4F) 4s^2 5D_3 + (4F) 4s^2 5D_5$
	12	56.65 (5)		
	13	60.462 (5)		
	14	60.674 (7)		
	15	60.911 (6)		
	16	61.134 (5)		
17	61.368 (10)			
18	61.527 (5)			
19	61.730 (10)			
20	61.880 (5)			
21	62.090 (5)			
22	62.222 (10)			
23	62.356 (10)			
24	62.547 (8)			
25	62.772 (10)			
26	62.886 (10)			
27	63.077 (10)			
28	63.497 (10)			
29	63.665 (10)			
30	63.802 (10)			
31	63.930 (15)			

Table 1. (cont'd)

Element	Peak	Energy (eV)	Absolute error (eV)	Assignment
Co	1	57.098 (10)	.035	Co $3p^6 3d^7 4F_{9/2} +$ $+ 3p^5 (2P) 3d^8 (3F) 4G_{11/2}$
	2	57.586 (15)		$+ (3F) 4G_{9/2}$
	3	61.5 (1)		$+ (3P) 4D_{7/2} + (3F) 4F_{9/2} +$ $+ (3F) 4F_{7/2} + (1G) 2G_{9/2}$
	4	63.0 (2)	.050	$+ (3F) 4D_{7/2}$
	5	66.933 (8)		
	6	67.258 (8)		
	7	67.570 (8)		
	8	67.760 (20)		
	9	68.000 (8)		
	10	68.150 (15)		
	11	68.360 (15)		
	12	68.750 (10)		
	13	68.867 (20)		
	14	69.100 (20)		
	15	69.370 (20)		
	16	69.762 (30)		
Ni	1	64.35 (10)	.05	
	2	65.35 (15)		
	3	68.55 (15)		
	4	74.200 (17)	.06	
	5	74.625 (25)		
	6	75.272 (17)		
	7	75.680 (17)		
	8	76.130 (28)		
	9	76.520 (25)		
Cu	1	73.15 (5)	.06	Cu $3p^6 3d^{10} 4s^2 2S_{1/2} +$ $+ 3p^5 (2P_{3/2}) 3d^{10} 4s^2$
	2	75.40 (5)		$+ 3p^5 (2P_{1/2}) 3d^{10} 4s^2$
	3	79.80 (8)	.07	$+ 3p^5 (2P_{3/2}) 3d^{10} 4s 5s$
	4	82.13 (8)		$+ 3p^5 (2P_{1/2}) 3d^{10} 4s 5s$
	5	84.13 (10)		

Figure Captions

- Fig. 1 3p-absorption of atomic (solid line) and metallic (Sonntag *et al.* 1969, Haensel *et al.* 1968) (dashed line) Fe, Co, Ni and Cu. The spectra calculated by Davis and Feldkamp (1976) for metallic Fe, Co and Ni are given by the dotted line. By shifting the theoretical curve in energy the minima at the 3p-threshold have been aligned.
- Fig. 2 Absorption of atomic Fe at the 3p threshold (solid line). The calculated spectrum $Fe\ 3p^6 3d^6 4s^2\ ^5D_4 + 3p^5 3d^7 4s^2\ (J = 3, 4, 5)$ is included. The 3p excitation spectrum for a $3d^6$ core calculated by Davis and Feldkamp (1976) is given by the dotted line. The theoretical curve has been shifted in energy to give best agreement with experiment.
- Fig. 3 Absorption of atomic Co at the 3p-threshold (solid line). The calculated spectrum $Co\ 3p^6 3d^7\ ^4F_{9/2} + Co\ 3p^5 3d^8\ (J = 7/2, 9/2, 11/2)$ is included (Combet Farnoux 1974). The 3p excitation spectrum for a $3d^7$ core calculated by Davis and Feldkamp (1976) is given by the dotted line. The theoretical curve has been shifted in energy to give best agreement with experiment.
- Fig. 4 Absorption of atomic (solid line) and metallic (dashed line) (Sonntag *et al.* 1969, Brown *et al.* 1971) Ni at the 3p-threshold. The dotted line gives the spectrum obtained by adding the theoretical 3p excitation spectra for $3d^8$ and $3d^9$ cores given by Davis and Feldkamp (1976) weighted by their thermal population. The theoretical spectra have been shifted in energy to give best agreement with experiment.
- Fig. 5 Absorption of atomic (solid line) and solid (Sonntag *et al.* 1969) (dashed line) Cu at the 3p-threshold. The energy levels of atomic Zn, aligned at the Cu 3p-threshold, are given for comparison.

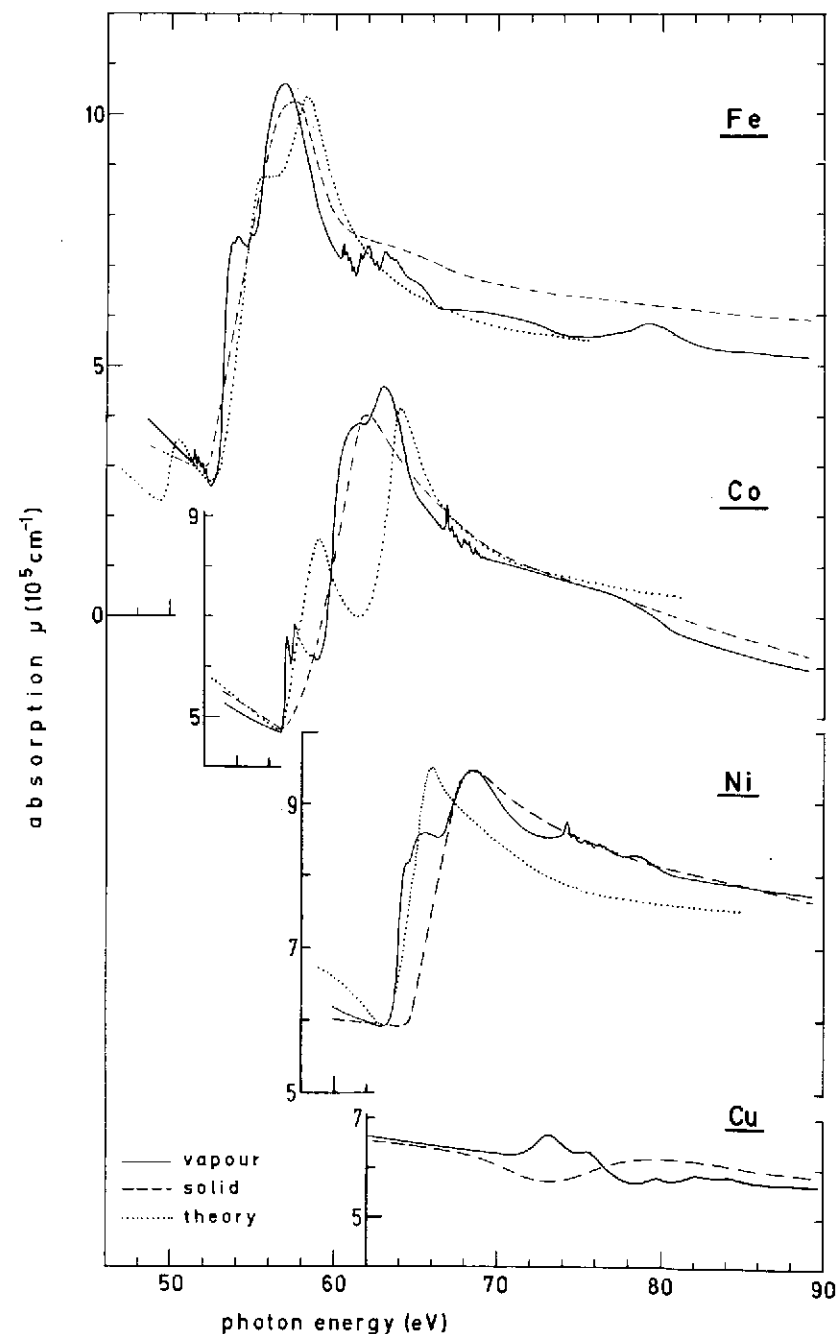


Fig. 1

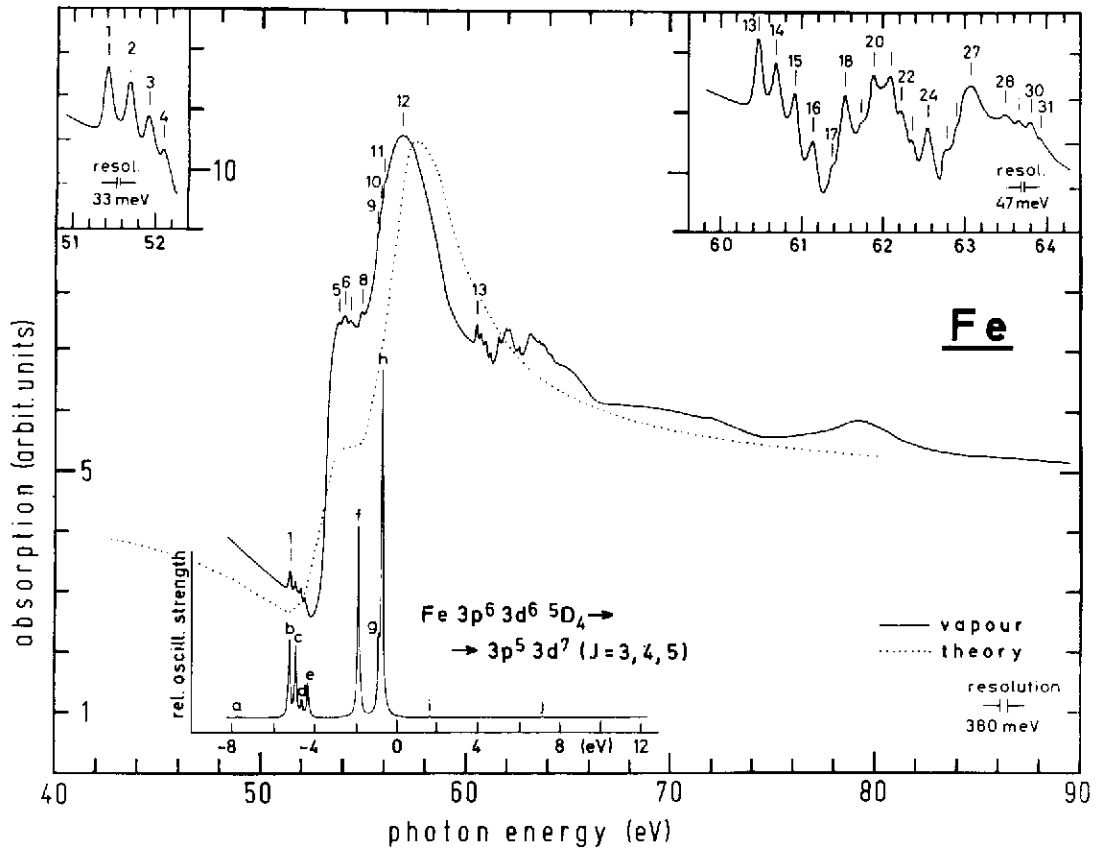


Fig. 2

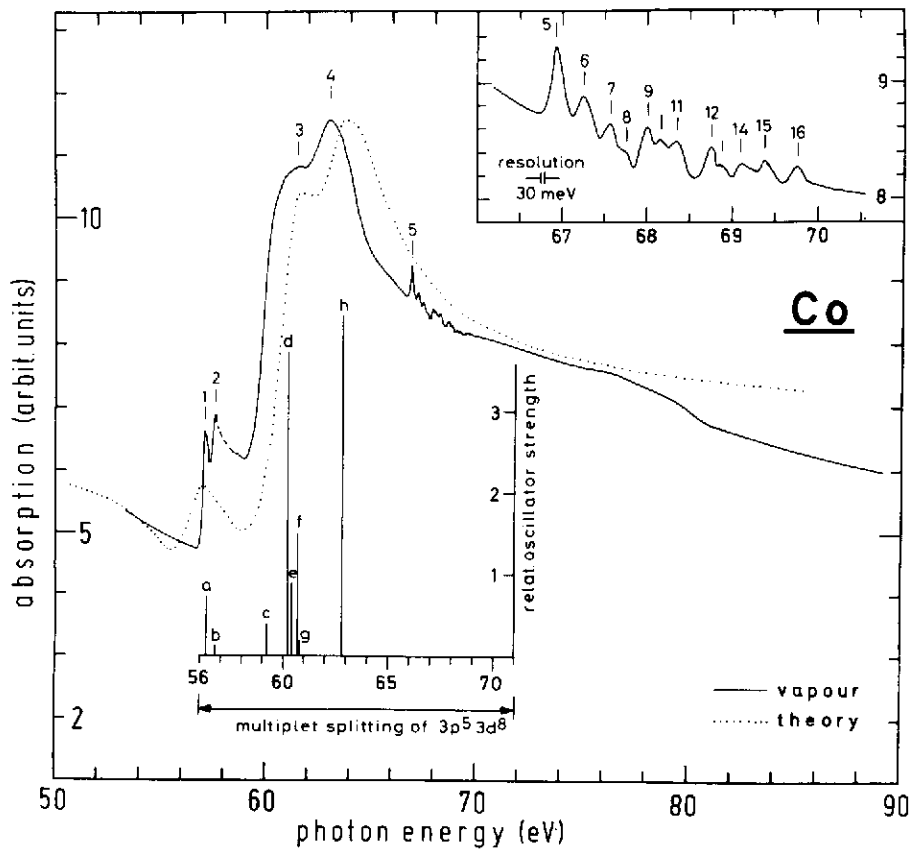


Fig. 3

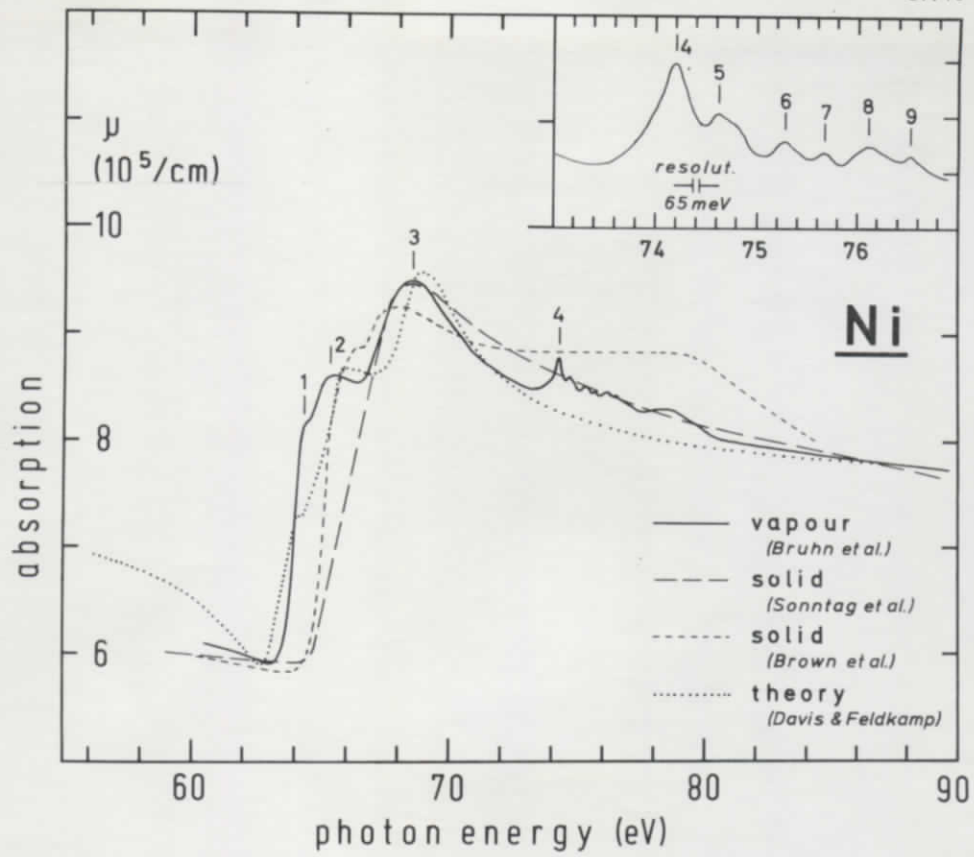


Fig. 4

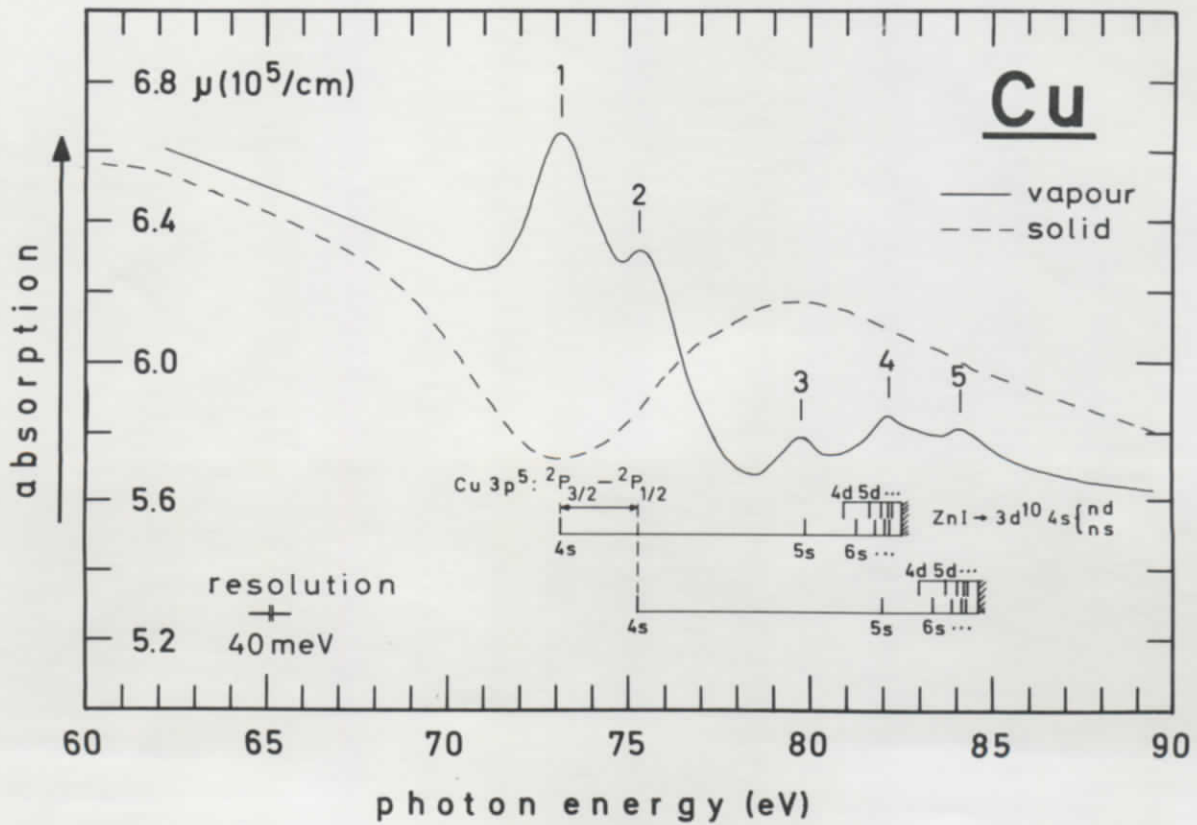


Fig. 5

