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The absorption spectra in the soft x-ray range show features which are commonly not found in the ordinary x-ray region. Several typical shapes of the absorption are discussed with examples of measurements which were obtained with synchrotron radiation from the 7.5 GeV electron accelerator DESY. The shift of oscillator strength to higher energies and the frequent absence of edge discontinuities is discussed with Au as an example. The atomic calculations give good overall agreement but are unable to explain broad prominent peaks in several light metals (Na, Mg, Al). Moreover, in these metals the electron hole interaction gives rise to a prominent narrow peak near the edge. Interchannel interaction appears to have an important influence on transition metal spectra (Ti to Ni).

1. Introduction

During the past few years a considerable effort has been made to diminish the gap in our knowledge of the absorption coefficient between the x-ray range and the UV range for a variety of materials. This progress is due, to a large extent, to the use of electron synchrotrons as light sources¹ by groups at the NBS, in Tokyo, in Frascati, at DESY and, more recently, at the storage ring in Wisconsin. Preparations of experiments at other places are in progress. Although excellent work has been done in the past and is still being done using conventional light sources the special properties of synchrotron radiation allow us to obtain data much more easily and faster and in many cases also more reliably.

In this paper we are going to focus our attention on three features which are characteristic for this spectral range, namely the shift of oscillator strength away from the edge to higher energies (Section 2.), a possible interchannel interaction in the spectra of the transition metals (Section 3.) and the "spike problem" in light metals (Section 4.). The experimental material shown are results obtained by the DESY group during the last few years.

2. Distribution of oscillator strength

The experiments in the soft x-ray region show that the most usual shape of the absorption coefficient is not the "saw-tooth" structure well known from the ordinary x-ray range. The oscillator strength from a new shell almost never assumes its highest value at the onset and, in many cases, the edge discontinuity is not even observed. Calculations of the transition probabilities in terms of realistic one-electron wave functions (instead of hydrogenic wave functions) for this intermediate energy range are in good

agreement with the experimental results. A thorough discussion is found in a review by Fano and Cooper.² The atomic calculations are a good first approximation, even for solids. Measurements for a variety of metals demonstrating this behaviour are now available, for example: tin³, gold^{4,5}, copper⁵, silver⁵, bismuth^{5,6,7}, the transition metals titanium to nickel⁸ and several transition metals in the group tantalum to platinum^{9,10}.

Since other papers at this conference give a detailed treatment of this topic we shall here only deal with one special aspect. A useful quantity, both to check the consistency of results and to learn which subshells contribute to the absorption in which energy range is the effective number of electrons which have contributed up to a certain photoenergy:⁵

$$(1) \quad N_{\text{eff}}(E) = \frac{mc}{\pi e^2 L h} \cdot \frac{A}{\rho} \int_0^E \mu(E') n dE'$$

with Avogadro's number L , atomic weight A , density ρ and the real part of the index of refraction n . In our range of interest $n \approx 1$ holds.

Figure 1 demonstrates this with Au⁵ as an example^{5,11}. The upper part gives μ with the core level binding energies marked. It is remarkable that no sharp edges are observed at these energies though tests have shown that discontinuities exceeding 5 % would have easily been detected. There is good agreement in the overlapping region with measurements by Jaeglé and Missoni⁴ and also fair agreement with atomic calculations by Manson and Cooper¹² which give results almost identical to those of Combet-Farnoux and Héno¹³. The N_{eff} curve, which includes results of other authors¹⁴ in the low energy region, shows a first saturation between about 100 and 200 eV at a value of $N_{\text{eff}} \sim 19$ which would be expected from counting all the electrons in the

conduction band, and the 5d-, the 5p-, the 5s-bands but not the 14 4f-electrons. The 4f electron transitions become possible above about 80 eV but, as demonstrated also by the theoretical calculations, their contribution becomes effective only after the minimum in μ at ~ 150 eV.

Although only a strict sum rule $N_{\text{eff}}^{(\infty)} = Z$ (where Z is the total number of electrons per atom) holds, and transfer of oscillator strength from one to another shell is theoretically possible, a naive and sometimes somewhat intuitive application of a partial sum rule as exemplified above has proved to be almost always successful. Table 1 gives a comparison for several metals.

Figure 2 shows¹⁵ the $L_{\text{II,III}}$ spectra of the light metals Na, Mg, and Al and the K-spectra of Li and Be, where prominent edge discontinuities occur. The region near the edge will be discussed in Section 4. Here we only point at the prominent peaks a, b, c which show a great similarity between the metals Na, Mg and Al. Atomic calculations, as indicated in the spectrum of Al, only give the general shape and according to Cooper¹⁶ there is almost no hope that a refinement of the atomic theory could reproduce these maxima. However, solid state effects could be responsible for this structure.

Another possible interpretation originates from the so called "plasmaron"-theory¹⁷ which demands the excitation of collective modes simultaneously with the excitation of the core electron. This theory correctly described¹⁸ the position of these peaks for Al. (The comparison was made with the measurements of Fomichev¹⁹, with which we are in full agreement.) However, this theory fails to correctly give the positions of these peaks for Na and Mg.

3. Transition metals

In the transition metals Ti to Ni the 3d-band with a width of ~ 4 eV is continuously filled until it is completely occupied in Cu. This picture, the rigid-band model, might need many refinements but the order of magnitude of the total bandwidth is a well established parameter. When we began investigating the 3p electron transitions in these elements we expected to see an image of the empty 3d states, namely a peak in the absorption spectrum which would have a width of about 4 eV for Ti and decrease to zero width in Cu. The curves⁸ (Fig. 3) indeed show a peak but its width for Cr is about 25 eV and although the width is smaller for the elements Mn, Fe, Co the shape is very unusual.

After these results had been published Fano and Cooper²⁰ came up with a reasonable explanation for this behaviour: for example, the spectrum of Mn appears to show, not just a peak which is superimposed additively onto a background, but a suppression of this background before the pronounced rise. This indicates that an interference takes place between the strong background and the superimposed line resulting in an asymmetric line shape.

This so-called interchannel interaction has been observed extensively in the rare gas spectra² where autoionization lines are superimposed onto a continuous background and we have also recently demonstrated this effect in solid rare gases.²¹ In the case of the transition metals this interaction would not only account for the unusual line shapes but also for the broadening of the peaks. More recently, we have found indications of similar behaviour in the $O_{II,III}$ -spectra¹⁰ of Ta, W, Re, and Pt.

Figure 4 shows a comparison of the $M_{II,III}$ structure shown in Fig. 3 for Ni and Fe with the L_{III} absorption structure measured by Bonnelle²². For both metals the L_{III} structure has a width which agrees much better with what is expected to be the width of the empty d states. This could have its explanation in the absence of a strong continuum under the L_{III} peak.

4. Edge anomalies

One of the necessary assumptions needed to explain the existence of sharp absorption edges is that the conduction electrons in a metal completely shield the coulomb potential originating from the hole in the atomic core shell. This cannot be perfectly true since the shielding can only be good down to distances in the order of about 1 ÅU in a good metal. Recently, the influence of the unshielded part of the hole potential on the excited electron and the other metal electrons has been treated thoroughly both for emission and absorption in several theoretical papers²³. If the core level is a p-state the result is a singularity of μ at the edge. The shape of the cross section in the region immediately following the edge is:

$$(2) \quad \mu \propto \frac{1}{E^\alpha}$$

ΔE is the distance from the edge and α is a positive exponent equal to ~ 0.5 . (Actually a prominent peak rather than a singularity is expected due to Auger and temperature broadening.) On the other hand no singularity should occur at the onset of s-electron transitions. For these transitions α is expected to be negative but of small absolute magnitude.

Already in Fig. 2 a prominent peak (a "spike") is recognized at the edges of Na, Mg and, less pronounced, at the edge of Al. Figure 5 shows the edge

regions of all the metals shown in Fig. 2 on an expanded scale^{24,25}. It is now clearly seen that it is a peak right at the edge for the $L_{II,III}$ spectra. (A splitting into two peaks A and A' arises from the spin orbit splitting of the ground state.) No such peak right at the edge is seen in the K spectra of Li and Be. Indeed, Li appears to show a softening of the edge which would match Eq. 2 with $\alpha < 0$, but the width of this edge could as well be caused by life-time broadening. A recent measurement²⁶ of the temperature dependence showed no change of the shape of the absorption edge between room temperature and liquid helium temperature. Results of other groups on Al^{27,28} and Mg²⁷ agree well with ours.

The theoretical results are complementary in emission and absorption and, indeed, also the emission spectrum of e.g. Na²⁹ shows a frequently discussed peak at the edge. It should be mentioned though that the peaks in emission are much weaker than in absorption and the absolute magnitude of the spike has still to be calculated theoretically.

I wish to thank my colleagues at DESY, especially R. Haensel and B. Sonntag, with whom I have collaborated during the past years on these problems, for many fruitful discussions.

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Table 1: Comparison of experimental^{5,11} and theoretical N_{eff} -values.

	N_{eff}	N_{eff} experiment	energy range
Cu	19	18	0-500
Ag	19	22	0-370
Au	33	32	0-500
Sn	18	21	36-500
Bi	32	28...	40-500

Figure Captions

- Fig. 1 Absorption coefficient μ and number of effective electrons N_{eff} as functions of the photoenergy for Au
- Fig. 2 Absorption coefficient μ with the L contributions for Na, Mg, Al and the K contributions for Li and Be
- Fig. 3 Absorption coefficient μ for the elements Ti to Cu in the $M_{\text{II,III}}$ region
- Fig. 4 Comparison of the $M_{\text{II,III}}$ spectra of Fig. 3 and the L_{III} spectra after Bonnelle²² for Fe and Ni
- Fig. 5 Shape of the $L_{\text{II,III}}$ edges of Na, Mg, Al and the K edges of Li and Be

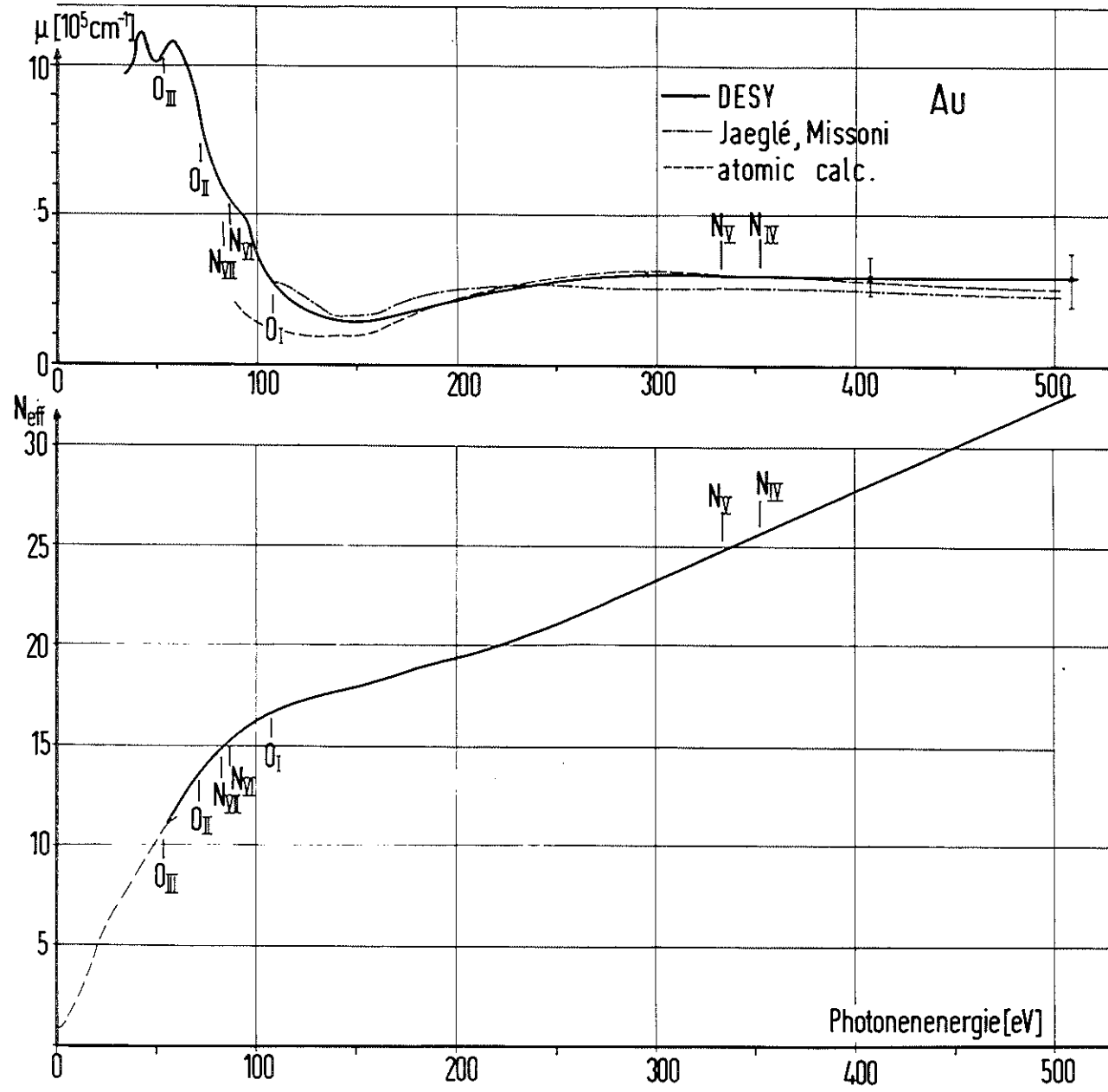


Fig. 1

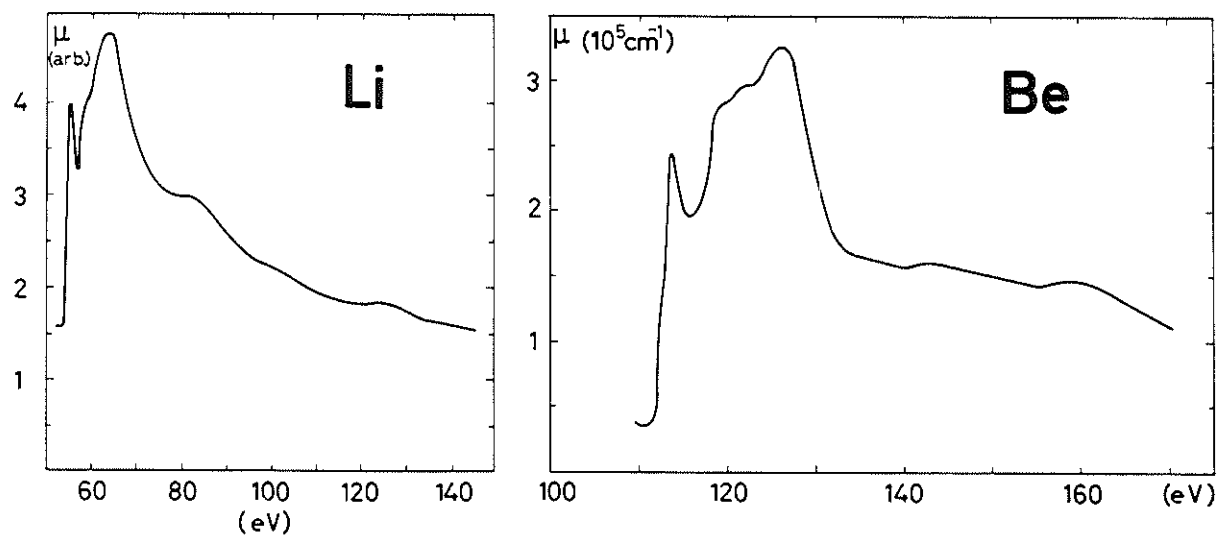
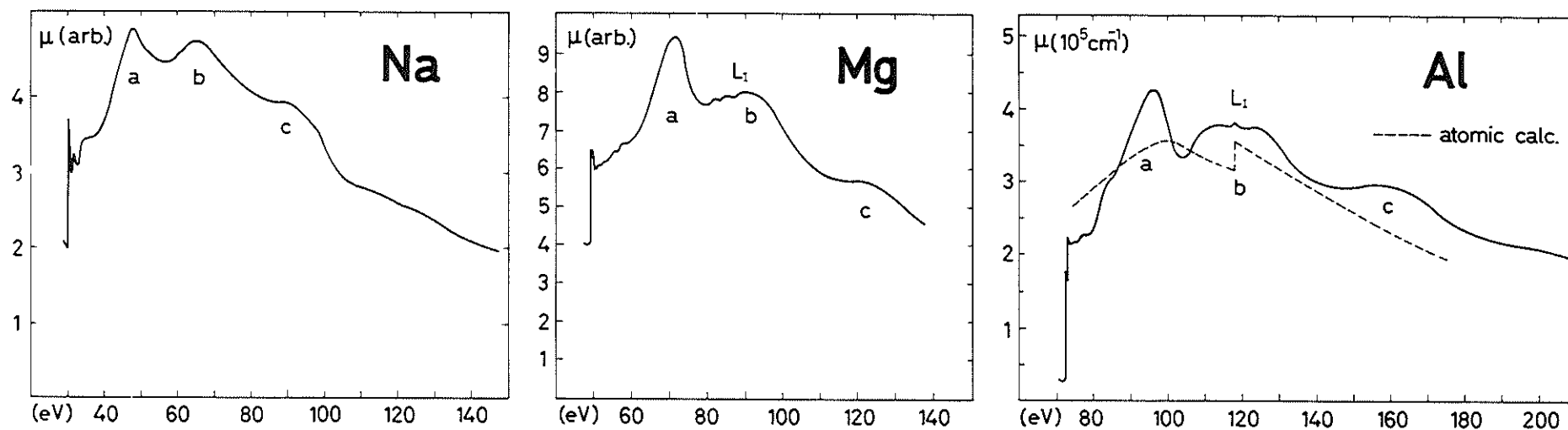


Fig. 2

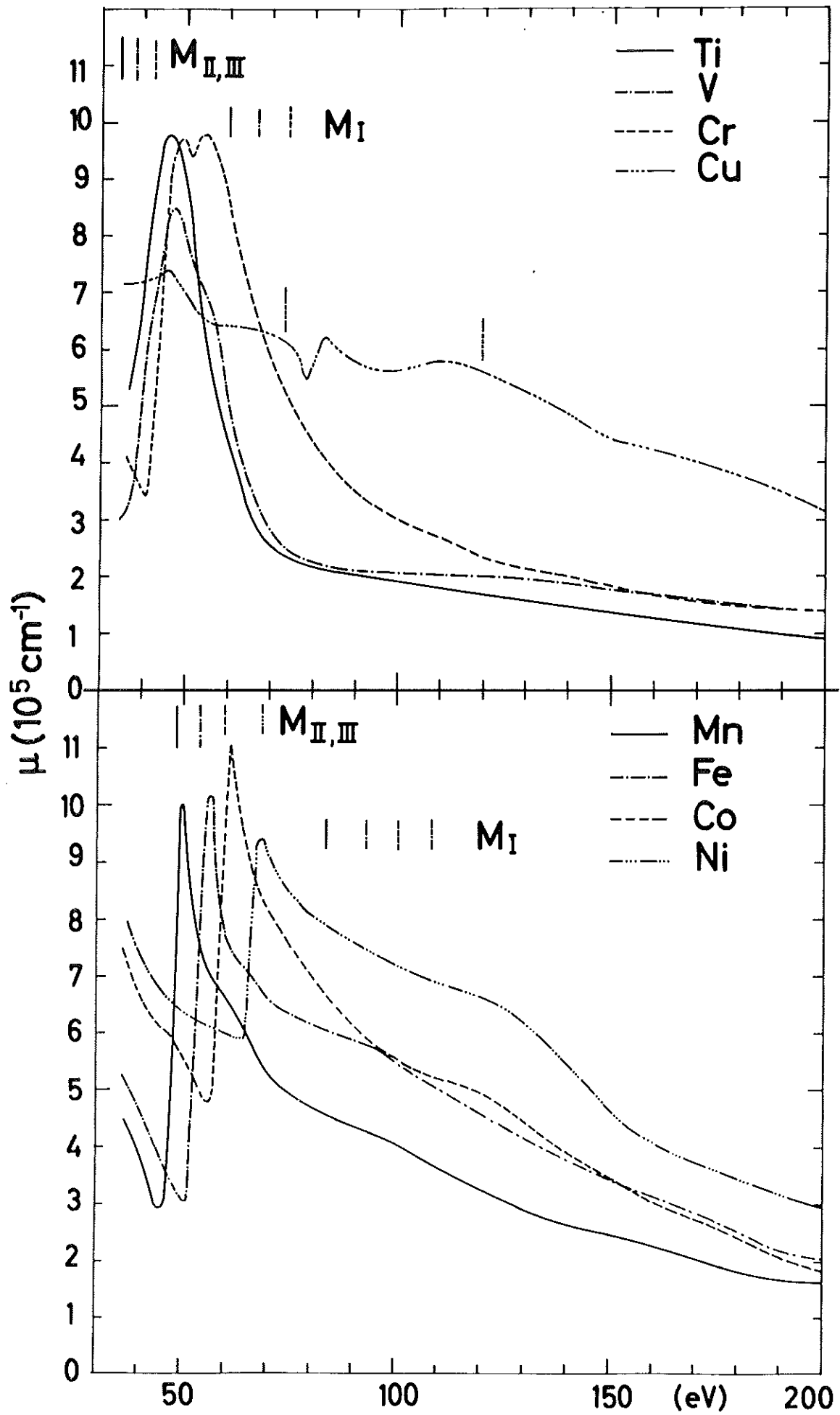


Fig. 3

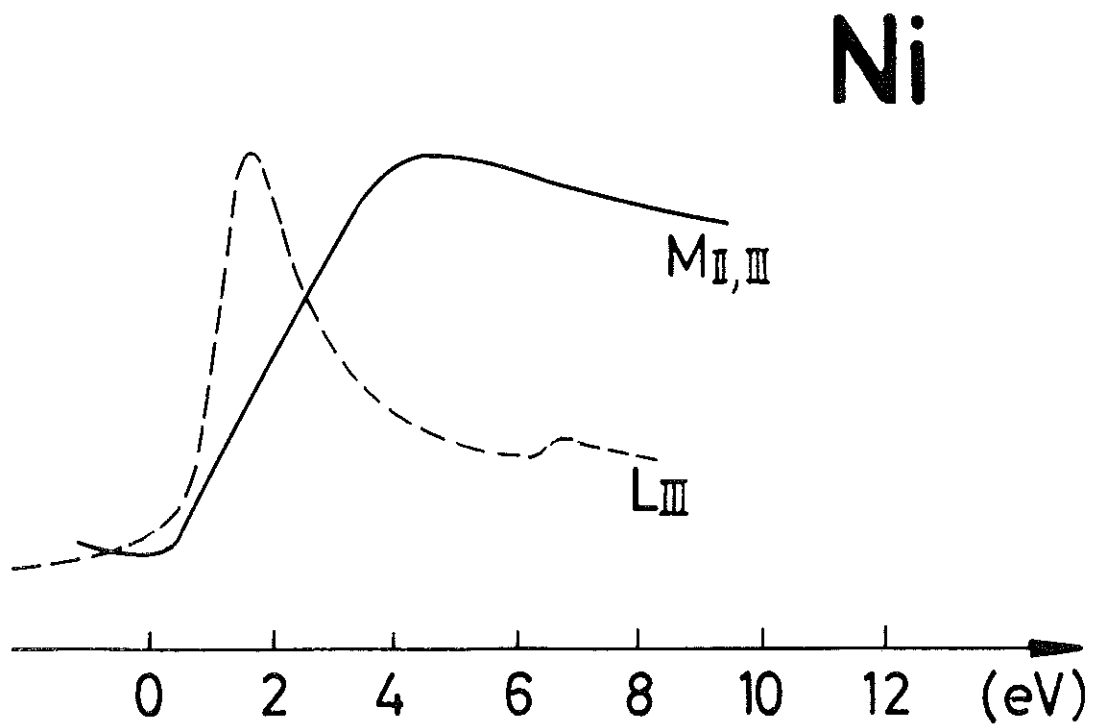
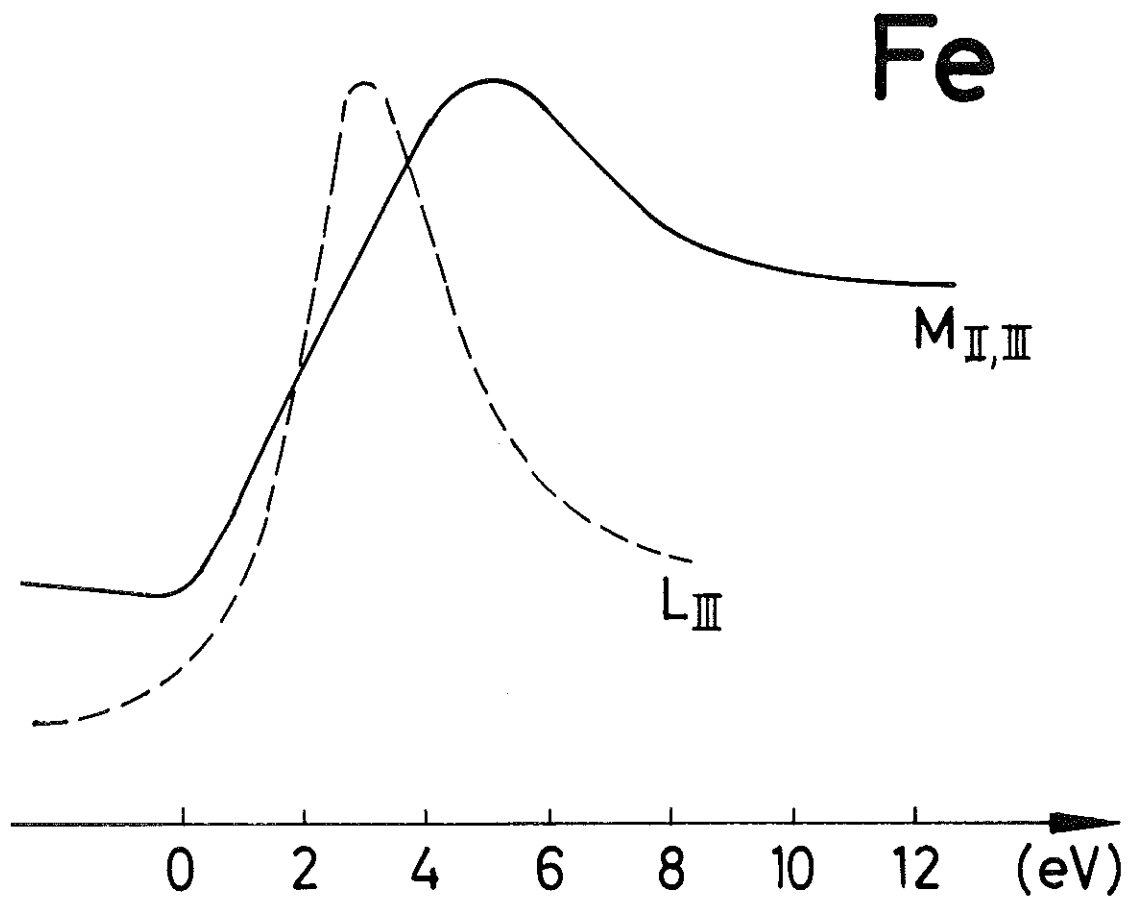


Fig. 4

Fig. 5

