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Ce AND La INTERMETALLIC COMPOUNDS
AND THEIR IMPLICATIONS FOR THE 4f
LEVELS OF Ce COMPOUNDS**

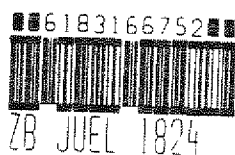
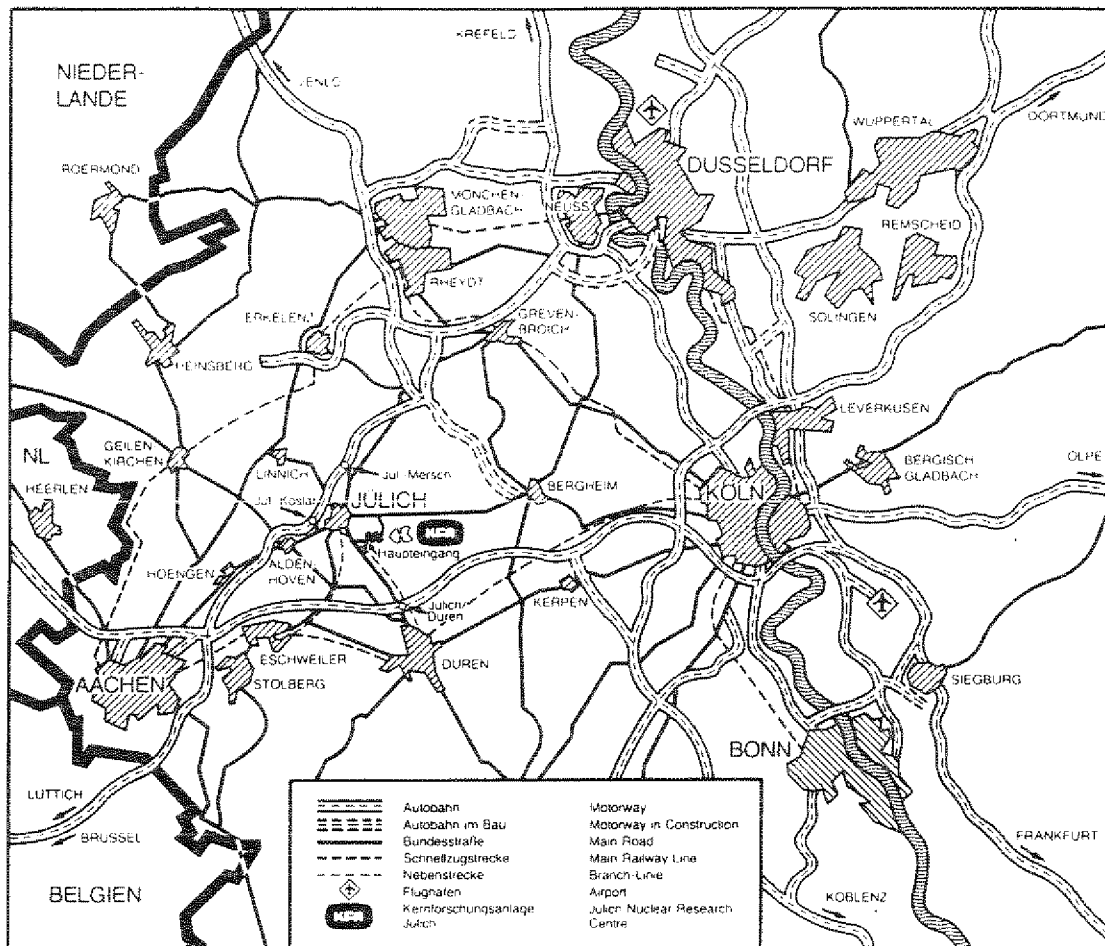
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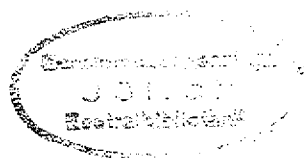
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CORE-LEVEL XPS STUDIES OF Ce AND La INTERMETALLIC COMPOUNDS AND THEIR IMPLICATIONS FOR THE 4f LEVELS OF Ce COMPOUNDS

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Zusammenfassung

Wir zeigen die Röntgenphotoelektronenspektren (XPS) der 3d Rumpfniveaus von ca. 30 intermetallischen Verbindungen von La und Ce. In einigen Ce-Verbindungen werden Übergänge in Endzustände mit näherungsweise f^0 -, f^1 -, und f^2 - Charakter beobachtet (f^0 und f^1 bei La-Verbindungen). Wir diskutieren die Resultate im Rahmen neuerer Anschauungen über den Einfluß der f-Zahl und der Hybridisierung des f-Niveaus auf die Linienform des Rumpfniveaus. Wir können die beobachteten Spektren nicht mit dem geläufigen "promotional model" in Einklang bringen, bei dem die f-Zahl stark variiert, und das für einige Verbindungen zu der Schlußfolgerung führt, daß das 4f-Elektron vollständig in das Ce 5d6s Valenzband transferiert wird. In Verbindung mit Vorstellungen über Abschirmprozesse in XPS entnehmen wir aus der beobachteten Linienform, daß die Kopplung des 4f-Elektrons an Kontinuumszustände in denjenigen Verbindungen am stärksten ist, denen früher im f^0 Grundzustand zugeordnet worden war. Die Kopplung wächst an, wenn das Ce mit Ni und Pd verdünnt wird, obwohl dabei der Abstand zwischen zwei Ce Atomen stark anwächst. Dieser Effekt kann daher nicht von einer direkten f-f-Wechselwirkung herrühren, und muß auf Kopplung an die anderen Valenzelektronen zurückgeführt werden, sogar möglicherweise an die des Legierungspartners. Wir diskutieren die Konsequenzen dieser Kopplung, bzw. Hybridisierung des 4f-Niveaus; außerdem wird ein Modell erörtert, das - obwohl sich ein relativ scharfer f-Zustand durch die Fermi-Energie bewegt - keine großen Änderungen der f-Zahl aufweist. Eine früher vernachlässigte Linienverbreiterung wird untersucht; sie erreicht in einigen Fällen 3 eV. Wir interpretieren diesen Effekt als eine Wechselwirkung zwischen dem Abschirmniveau, das als ein virtuell gebundener Zustand anzusehen ist ("virtual bound state"), und den anderen Valenzzuständen. Dieser neue, an XPS Rumpfniveauspektren beobachtbare Effekt könnte unter einigen Voraussetzungen ein direktes Maß für die Wechselwirkung zwischen den f-Zuständen und den anderen Valenzzuständen liefern.

Abstract

The 3d core hole x-ray photoelectron spectra (XPS) of approximately 30 intermetallic compounds of La and Ce are reported. Transitions to final states with approximately f^0 , f^1 and f^2 character are observed in some Ce compounds (f^0 and f^1 for La compounds). The results are discussed in terms of the current ideas of the influence of f -counts and f -level hybridization on core level lineshapes. We cannot find an explanation of the observed spectra consistent with the "promotional model" where the $4f$ -count varies and $4f$ electron was thought to be entirely promoted to the Ce $5d6s$ valence bands in some compounds. There may be some small charge transfer from the f level, however. In conjunction with ideas on screening processes in XPS the observed lineshapes suggest coupling of the $4f$ electrons to other states is strongest in those compounds previously thought to have f^0 character. This coupling increases despite a large increase in the Ce-Ce distance when Ce is diluted with Ni or Pd. Thus it cannot be due to direct f - f interaction and must be attributed to coupling with the other valence electrons; possibly those centred on the partner sites. The implications of this coupling, or hybridization of the $4f$ levels, and a model which allows a fairly sharp f level to pass through the Fermi level without large f -count changes, are discussed. A previously ignored peak broadening is investigated and found to be as large as ~ 3 eV in some cases. It is attributed to interaction between the screening level, which is a virtual bound state, and the other valence levels. It is thought that this new core level effect may eventually yield a direct measure of the strength of the interaction between the f states and other valence states.

INTRODUCTION

In this paper we will present the 3d core level x-ray photoelectron spectra (XPS) from ~ 30 intermetallic compounds of La and Ce and discuss their implications for the structure of the 4f levels in the valence and conduction bands. These investigations were made against a background of general confusion about the role of the 4f electrons in Ce and Ce compounds /1,2/. We will show that f level hybridization with the other valence levels in Ce and its intermetallics is important. The f level width inferred indirectly from core level spectroscopy, is more dependent on the chemical environment than on the Ce-Ce distance.

The conventional picture for the role of the 4-f level in Ce compounds was based mainly on lattice constant and magnetic measurements and is summarized with the help of figure 1 which has been adapted from reference 3. The basis of that classification was that the f-level in Ce had a width of ~ 20 meV or less and was close to the Fermi level. This f level could be empty, with an f electron promoted to the s-d valence band to give a "valency" of 4, or below the Fermi level and singly occupied to give a "valency" of 3. It was thought that in some compounds the narrow f level was at the Fermi level and a non-integral f count, or configuration fluctuation, or mixed valence resulted, as in some heavy rare earth compounds /4-7/. Whilst some authors might argue for small changes in the boundaries between the regions, the basic suggestion was that in compounds with elements in region A of figure 1, Ce had an f-count below 1 i.e. Ce had a "valence" greater than 3, and for A-richest compositions tetravalent Ce (f-count=0) would be found. It was also thought that B elements formed compounds with Ce in intermediate states (f-count between 0 and 1) and with C-elements the

valency of Ce would be 3 /3,6,7/. We cannot explain our core-level XPS results within these schematics and will suggest that other descriptions of the 4f electrons may be more appropriate. In view of our difficulties with the so-called promotional model described above it is sensible for us to consider some of the evidence for and against f-count changes in Ce and its compounds and to pinpoint some ambiguities.

Ce itself undergoes a phase transition on cooling under pressure from a magnetic γ form to a non-magnetic α form with a concurrent volume collapse of $\sim 16.5\%$ /8-10/. Historically this collapse was first attributed to (partial) excitation of a 4f electron to the valence band in the α phase /9,10/ so that the Ce configuration changes. Arguments against this promotional model were put forward about ten years ago /11,12/ (see also references 1-7,13,14) partly on the basis of thermodynamic arguments: it was suggested that the α - γ transition might be related to a Mott transition. Compton scattering /15/ and other experiments /6/ now give convincing evidence that the promotional model was not appropriate to the α - γ Ce transition and that the 4f-count does not vary much in between α and γ -Ce. However, there are some arguments against the Mott transition, for instance that a true Mott transition would be due to f-f overlap and that Ce diluted in Sc shows phenomena like pure Ce although the Ce-Ce distance is dramatically increased /16/. Recent suggestions for the origin of the α - γ phase transitions and similar effects include Kondo-like effects (see e.g. refs. 11, 17-20) and a second well in the potential of the Ce 4f electrons so the 4f wave function has considerable amplitude at the Wigner-Seitz cell boundary /21/.

The intermetallic compounds of Ce also show unusual variations in lattice parameters, magnetic susceptibility, specific heat, and neutron scattering effects. This has also led to some dispute about whether the f -count varies in Ce compounds. Observations that have been cited as evidence for f -count variation include the following: Ce compounds with C group elements such as Zn, Ag, Au show ferro-or anti-ferromagnetic ordering at low temperatures due to a nearly localized $4f$ electron /6,7/. Also the compounds of Ce with these elements have lattice constants which agree with the value obtained by interpolation from the analogous La and Pr compounds which are known to be always three-valent. Thus in the f count-variation model these Ce compounds have f^1 Ce. A-group elements such as Ni, Fe, Co, Ru, Rh, Os, or Ir have anomalously low lattice constants with respect to the corresponding La or Pr compounds, consistent with the presence of the smaller Ce^{4+} ions, and in many cases there is no magnetic ordering at low temperature in the intermetallics with low Ce content. Some of these intermetallics also show superconductivity at low temperatures /22/. It has thus been implied that these compounds have pure $Ce f^0$ configurations, especially the intermetallics with low Ce content. A third group of compounds, such as CeN, $CePd_3$, and CeAs also show low lattice constants by comparison with the corresponding La or Pr compounds, but not low enough to imply the presence of Ce atoms in the f^0 configuration. Also such compounds exhibit anomalous magnetic and specific heat properties at low temperatures similar to those found in homogeneous mixed valence of Sm or Yb. This led to the postulation of mixed valence in these Ce compounds with, non-integral f -counts, and a narrow $4f$ level (width $W < 0.1$ eV) pinned at E_F . Indeed neutron scattering results of, for instance $CePd_3$, were rationalized in terms of a half-filled Ce $4f$ level with a width of ~ 20 meV /20,23/. XPS-BIS measurements at

first sight support this picture although they do not indicate such small f widths /24,25/. Despite this evidence there are arguments against the concept of a narrow $4f$ band ($W < 0.1$ eV) in Ce compounds that may be positioned below, at, or above E_F depending on the chemical environment, so that the f -count varies from zero to one. As in the case of the α - β Ce transition, thermodynamic arguments are against large variations in occupancy of a narrow $4f$ level /13,14/. Also Allen et al. /26/ and Peterson et al. /27/ have used Fano resonance photoemission studies of Ce intermetallics to pick out the Ce $4f$ emission and have interpreted their data as an indication that the f count is never zero in intermetallic compounds and the f -widths are quite large and a similar conclusion has been reached from core level XPS studies /28, 31/. It may also be argued that the absence of a localized magnetic moment in some Ce intermetallics may be due to hybridization effects, and not a zero f -count. Further, spin-relaxation time effects indicate that the mixing of Ce $4f$ with other wave functions is much larger than for the f levels in heavier lanthanides /29/.

Photoelectron spectroscopy of the valence band is not an ideal probe of the Ce $4f$ electrons because of their small cross section. In separate papers we have placed great emphasis on the fact that core level spectroscopies are also not a panacea that will immediately resolve all of the above contradictions /24,28,30-32/. A picture has evolved in which $3d$ core ionization of La or Ce compounds results in a spectrum of final states whose configurations correspond roughly to f^0 , f^1 and f^2 . As the core hole is energetically better screened in the final states with higher f count, the XPS peaks corresponding to transitions to those states are at lower binding energy /28,30-42/ as indicated in figure 2 for $3d$ core hole creation. In general the intensity of the core

lines is spread amongst final states with different f -counts in Ce compounds whilst for heavier rare earths this tends to be true only for mixed valence compounds /28,30-43/. However, there are exceptions even amongst heavier rare earths (see e.g. reference 44). Note also that we deliberately avoid giving any of the states in figure 2 integral f -count. The exact f -count is not known for any state, but recognition of the possibility of variations from integral values due to hybridization is important.

We choose to study the 3d region of the XPS spectrum because of the high cross section for 3d ionization /45/, because broadening due to the core hole lifetime is manageable, even if significant (1.5-2 eV /46,47/) and because the multiplet splitting due to interaction between a 3d hole and unpaired 4f electrons is not too large in light rare earths /48,49/. These considerations outweigh the disadvantage that splitting due to different f -counts is comparable to the 3d spin orbit splitting so that for Ce there is some overlap between the $3d_{3/2} 3d^9 4f^2$ and the $3d_{5/2} 3d^9 4f^0$ peaks. We illustrate the spectra with the example of $CeNi_5$ in figure 3. This figure indicates for the case of $CeNi_5$ that the peaks due to f^0 , f^1 and f^2 like final states can be identified and their experimental intensities can be measured with reasonable accuracy. The relative intensities of the so-called f^0 , f^1 and f^2 peaks in 3d XPS spectra does not, in general, give directly the amplitude of f^0 , f^1 , and f^2 like wave functions in the ground state /28,30,32/. However, as the peak due to the $3d^9 4f^0$ final state is 10 eV to higher BE than the $3d^9 4f^1$ or $3d^9 4f^2$ peaks we can assume that the $3d^9 4f^0$ state does not strongly mix with the others. In the absence of such mixing the $3d^9 4f^0$ peak intensity would give the $4f^0$

amplitude in the ground state /28/ but we do not propose that such mixing is completely absent.

In an alternative and in many ways equivalent, description of these phenomena we say that one must consider the dynamics of screening and photoemission /31,50-55/. In this latter description one says that in the ground state with approximately n 4f electrons ($n=0$ for La, 1 for Ce) there is a $4f^{n+1}$ level at energy Δ_+ above E_F . Δ_+ is known from Bremsstrahlung isochromat spectroscopy to be approximately 4-5 eV in La and Ce or their compounds /21, 56/. When a 3d core hole is created the $4f^{n+1}$ level is pulled below E_F and can be filled by an electron from the (5d+6s) valence band to screen the core hole. The probability that the $4f^{n+1}$ level will be filled depends on its coupling to the rest of the system, i.e. on its width, W , arising from hybridization and its energy Δ_+ above E_F /31,50-52/. If coupling is strong and W/Δ_+ is large, then the probability of filling the $4f^{n+1}$ level on 3d ionization is large, so that the XPS peak at lowest energy, corresponding to a transition to the $3d^9 4f^{n+1}$ state, is large. If on the other hand, the $4f^{n+1}$ level is weakly coupled to the system, W/Δ_+ is small and more intensity is found in the higher energy XPS peak corresponding to the transition to the $3d^9 4f^n$ final state. Because of such effects it is not possible to determine the ground state f^n and f^{n+1} amplitudes from the $3d^9 f^n$ and $3d^9 f^{n+1}$ peak intensities (and to a lesser extent the f^{n-1} peak intensities in Ce compounds) but large intensities in the f^{n+1} and/or f^{n-1} XPS peaks do indicate a larger degree of hybridization of the 4f levels /28,31,50,51/.

In this paper we will present the 3d XPS spectra from a variety of Ce intermetallic compounds, to check on the effects of the f^0 wave function and hybridization in Ce compounds. Special emphasis will be placed on comparison with the corresponding La spectra. We will interpret the data to give semi-quantitative trends in f counts and f level hybridization. The implications of the La $3d^9 4f^0 - 3d^9 4f^1$ splitting for the 4f electron binding energy in Ce compounds will also be discussed using the $Z+1$ approximation. We will then discuss possible models that might bring together ideas arising from other techniques. Ce and La 4d XPS spectra are strongly affected by $4d^9 - 4f^n$ multiplet interactions and are not extensively discussed here.

As discussed above the situation in Ce is complicated and not all the concepts proposed in the literature can be right. In discussing our results we will try to return more to basics and use the following premises as a framework for our discussion.

1) There are no reliable estimates of the f -counts in Ce intermetallic compounds. In view of the controversies outlined above arguments for a fairly stable f -count of near 0 in La and near 1 in all Ce intermetallics deserve as much consideration as arguments that the f -count varies between 0 and 1 in Ce intermetallics.

2) The 4f electrons in Ce and its compounds are quite strongly localized because the effective Coulomb interaction between the 4f electrons, U_{eff} , is of the order of 6 eV and the Ce 4f band width, whilst not known accurately, is of the order of 1 eV or less.

3) There is evidence that the presence of valence levels that are strongly, but not completely localized leads to complicated core level lineshapes in XPS /28,30,55/. Core level photoemission cannot be described accurately in the one-particle approximation in such cases.

4) Quantitative values for f-counts cannot be derived directly from core level spectra because of configuration interaction and screening effects in the final state.

5) x-ray photoemission spectra may be described in the sudden approximation /7,58/. In this approximation the wave function of the system, Ψ_N is factorized into a one-particle and an N-1 particle, function. After photoionization the final states of N-1 particle system, $\Psi_i(N-1)$, are not identical to that of the initial state. The probability, p_i , of excitation to a given final state, $\Psi_i^*(N-1)$ is given by the overlap between the initial and final state wave functions i.e.

$$\text{i.e. } p_i = \langle \Psi_i^*(N-1) | \Psi(N-1) \rangle^2 \quad (1)$$

The sudden approximation is expected to break down when the photoelectron kinetic energy is small, but there is experimental evidence that it is quite good at the photoelectron energies relevant here /59,60/.

We organise our results in section III to first show how spurious effects such as extrinsic energy losses and Auger peaks were detected (section III_a). Data is then presented in III_b on La-Ni and Ce-Ni alloys as an example of compounds with an "A" group element as defined by figure 1. Sections III_c and III_d

contain the results on compounds with Pd and Sn (B-group elements) and Au (C-group elements) respectively. Section IV contains discussions of peaks shapes and multiplet effects (IVa), hybridization effects on the observed spectra (IVb) f-level widths and a comparison with other measurements. After a discussion of a suggestion that 4-f level positions can be deduced from core level spectra (IV e) we discuss models for the energy distribution of 4f character in the valence band (IV f).

II EXPERIMENTAL

The samples used in these studies were prepared by melting the components together in the required proportions using Rf heating in a cold crucible. The metals used were 4N or better, as specified by the producers - Johnson and Matthey or Hereaus. The samples were brittle and mostly air sensitive. They were cut into 1.7 mm slices by spark erosion and checked for the presence of secondary phases by metallography and x-ray diffraction. If necessary the samples were annealed for up to a week in vacuo to reduce the concentration of peritectic precipitates. No samples on which data is reported here contained more than 5% of impurity phases. All samples were stored in pyrex glass ampoules under vacuum or pure argon until use. Clean surfaces were obtained by scraping the samples in vacuo with an Al_2O_3 file. The level of O and C contamination, as judged by the O 1s and C 1s XPS peak intensities, did not exceed ~3 atomic % in the surface region. The measurements were made in an UHV photoelectron spectrometer custom built by Kratos U.K. Ltd. The instrument has typical operating pressures of 5×10^{-11} torr in both measurement and sample preparation chambers. AlK α x-rays from a home-made monochromator were used to excite the spectra. This monochromator has 54 quartz single crystals on a 1 m radius toroidal substrate to utilise a large solid collection angle /51/. In order to increase intensity the slits in the electron optics were opened which gave 600 meV total instrumental resolution. Reflection electron energy loss spectra were obtained by bombarding the samples with a primary beam from a Vacuum Generators LEG 22 electron gun and energy-analysing the (non-specular) backscattered electrons.

III RESULTS

a) Energy losses and Auger peaks

Until now literature accounts of core level XPS studies have mostly attempted to consider only the salient peaks without giving the underlying proof that these are the salient peaks. However, core level XPS spectra may contain contributions from energy loss processes and Auger peaks and we feel it is important to describe how their effects can be identified.

Many energy loss processes are extrinsic to the photoexcitation and are caused by inelastic scattering. Such processes may be detected by comparison with energy loss measurements in reflectance which only show extrinsic effects. In compounds the extrinsic loss structure is the same for the core levels of both components, which is a reasonable test for electron energy loss processes not restricted to one site (as intrinsic or "shake up" losses might be). In La, Ce, and CeAl_2 we suspected that peaks on the high B.E. side of the XPS core lines were due to energy losses and we will now show this to be true.

For La and Ce we compare the $3d_{5/2}$ XPS peak with the electron energy loss (ELS) features of backscattered electrons in figure 4. In the ELS spectra the features observed and listed in table 1 are definitely due to extrinsic features. The shape of the spectra are in reasonable agreement with those reflection ELS spectra recorded at 850°C in moderate vacuum by Zashkvara et al. /62/. Netzer et al. /63/ found the ~ 8 eV loss to dominate at low primary beam energy, and found increasing intensity in an ~ 12 eV loss at higher primary

beam energies. They find somewhat more intensity than us in a loss at ~ 12 eV with 1500 eV primary beams which may be due to the different geometry (near specular reflection) used by them. The feature g at ~ 28 -29 eV is assigned to an excitation with predominantly $5p \rightarrow 5d$ character whilst the feature d at ~ 12 eV is assigned to a bulk plasmon loss by comparison with heavier rare earths. The origin of loss c is difficult to understand as it is not present in heavy rare earths /63/ but it clearly important in interpretation of the XPS spectra.

The ELS spectra, taken at ~ 1500 eV primary beam energy, have been normalized so that the area of the primary ELS peak and the main $3d_{5/2}$ XPS peaks are the same. The intensity (height) of the ELS features in figure 4 is thus a guide to the strength of extrinsic losses in the XPS spectra, although the latter are less well resolved due to lifetime and multiplet effects. On the basis of this comparison we assign the features ~ 8 eV below the main XPS peaks (labelled c in figure 4) to extrinsic losses. The other ELS features are weaker and broader so that we cannot be as definitive about the role of the corresponding loss processes in the spectra. However, we draw special attention to the broad loss, labelled g, due to the $Ce 5p \rightarrow 5d$ excitation at about 29 eV in the Ce spectrum. A 29 eV loss from the main $3d_{5/2}$ peak is in the region where we look for $3d_{3/2} 3d^9 4f^0$ XPS peaks (see figure 3). In almost all Ce compounds we find a broad shoulder in this region of the XPS spectrum which we tentatively attribute to the loss labelled g. The true $3d^9 f^0$ peaks found in some compounds are sharper.

We note that the features labelled c, d, and c' were extremely sensitive to contamination, and were lost in the background at very low contamination levels.

The extrinsic losses in the XPS spectra were definitely more marked in the spectra from the cleanest samples, and their presence is a good indication of sample cleanliness.

In CeAl_2 we could use the Al 2p lineshape and satellites to detect inelastic losses. Figures 4 and 5 show the XPS spectra of the Al 2s, 2p, Ce 4d and Ce 3d levels of CeAl_2 . We attribute broad peaks occurring on the low kinetic energy side (high BE.) side of the Al as well as the Ce peaks of the spectrum to plasmon-like inelastic energy losses. For the Al 2p peaks the separation of the primary and loss peaks is approximately 14 eV, as compared to ~ 15 eV in Al itself /64/. As indicated in the figures all the high BE. "bumps" in the spectra can be explained as losses or multiple losses of a 14 eV quantum.

We have made a more quantitative study of these plasmon losses in CeAl_2 . In simple metals about 75% of the plasmon losses in the XPS spectrum are thought to arise from inelastic scattering (extrinsic losses), with the other 25% being due to simultaneous creation of photoelectrons and plasmon (intrinsic losses) (see e.g. references 22-24). It is reasonable to assume a similar ratio in CeAl_2 . The extrinsic loss probability is a slowly varying function of kinetic energy (KE.) so that it is the same for Ce 4d and Al 2p photoelectrons whose KE. differs by only approximately 2%. Although the intrinsic plasmon loss probability could be different for Ce 4d and Al 2p core hole creation the intrinsic plasmon loss probability is smaller and such differences do not contribute in a significant way to the total loss function. With these facts in mind we have used a procedure for subtraction of the losses from the spectra. Briefly it involves fitting the plasmon losses to a fold of the Al 2p primary

peak and a loss function and then stripping the losses from the spectrum point by point moving from low to high BE. The result is plotted in the lower part of figure 5. As seen, the procedure removes not only the Al 2p plasmon loss peak, but also most of the structure on the high BE. side of the group of Ce peaks, thus providing evidence for our assignment of the high BE. peaks to plasmon losses.

It is not valid to assume the same loss function for the Ce 3d and Al 2p photoelectrons as their kinetic energies differ by a factor of approximately 2.5. Subtraction of the Al 2p loss function thus yielded an unsatisfactory result with a "wavy" background on the high BE. side of the main peak, but we can certainly say that the $f^0:f^1$ peak ratio in CeAl_2 is less than 1:10.

The other extraneous effect in XPS spectra is Auger emission. This effect is detected by changing the primary x-ray energy which changes the KE. of the XPS peaks, but not the Auger peaks. In this case we used Mg $K\alpha$ radiation, to obtain the spectrum shown in figure 7 for La, where a large, broad, feature at ~ 622 eV KE is found to be independent of the x-ray energy used. This peak is attributed to the La $M_{4,5}N_{4,5}^{N_{4,5}}$ transitions and is present in all the XPS spectra of La compounds presented in this paper. In general no Auger peaks from other elements, such as Ce, Ni, Pd, etc. are expected to interfere with the 3d XPS emission and similar checks with Al $K\alpha$ and Mg $K\alpha$ radiation revealed no such Auger features.

b) La-Ni and Ce-Ni intermetallic compounds.

Ni compounds were chosen as examples of A-group compounds because the phase diagrams are quite well known /65/. The La 3d spectra of La-Ni intermetallic compounds, illustrated in figure 8 show overlap between the Ni $2p_{3/2}$ and La $3d_{3/2}$ peaks. As the Ni concentration is increased the Ni peaks grow and dominate the spectra in this region. As the spectra have been normalized to the intensity difference between the background at ~ 825 eV BE. and the La $3d_{3/2}$ Ni $2p_{3/2}$ peak at ~ 848 eV, the La $3d_{5/2}$ peak at ~ 835 eV decreases in intensity in figure 8. However, it can be seen that the well-screened $3d^9_{5/2}4f^1$ at ~ 831 eV is growing with respect to the $3d^9_{5/2}4f^0$ peak as the Ni concentration is increased. The precise energies of the XPS peaks are given in tables II and III and the estimated relative peak intensities are collected in table IV.

The Ce 3d spectra from Ce-Ni intermetallics are presented in figure 9 and here also the f^{n+1} (i.e. f^2) peaks grow in relative intensity as the Ni concentration is increased, indicating increased hybridization of the f levels. In the $CeNi_x$ compounds the f^0 peaks become distinct when $x > 1$ and increase in intensity as the Ni concentration increases. Before proceeding it is worth noting that the 4d XPS spectra of these Ce alloys contain strong evidence for the assignment of the peak at ~ 914 eV to $3d^9 4f^0$ final states. The $CeNi_x$ spectra in figure 10 have intensity due the $4d^9 4f^1$, $4d^9 4f^2$ final states and Ni 3s ionization in the region between 105 and 115 eV B.E. In addition two weak peaks grow up at ~ 120 eV in the Ce compounds with high Ni concentration. Their splitting is almost equal to the 4d spin orbit splitting in La /66/. They are unquestionably due to $4d^9 4f^0$ final states

because the $4d-4f$ interaction is strong and introduces strong multiplet effects in the $4d$ XPS peaks with complicated peak shapes that must be treated in intermediate coupling (see e.g. Refs. 41,66). The growth of the $3d$ peaks at ~ 914 eV parallels the growth of the $4d^9 4f^0$ peaks at ~ 120 eV and their separation from the main $d^9 f^1$ peaks is similar. Thus the ~ 914 eV peaks can safely be assigned to excitations to final states with mainly $3d^9 4f^0$ character.

In tables II and III we present the energies of the $3d$ XPS peaks corresponding to f^0 , f^1 and f^2 final states for the La and Ce compounds. It is noteworthy that the f^n-f^{n+1} peak separation remains constant in the La-Ni and Ce-Ni intermetallic compounds, but as will be seen later it varies as a function of stoichiometry in the Pd compounds. This is illustrated in figures 11 and 14 where the $3d_{5/2}$ peaks are shown on an expanded scale. We return to this point in section IV e.

c) La and Ce intermetallic compounds with Pd and Sn

The anomalous properties of $CePd_3$ are often attributed to mixed valence /1-6,23,69/. $CeSn_3$ also has many unusual properties that are not well understood and have been attributed to mixed valence /1-6,70-72/ and the compound does have a lattice constant anomaly /70/. These materials are thus suitable candidates for studies of B-group compounds. Figures 12 and 13 show the $3d$ XPS spectra of $LaPd_x$ and $CePd_x$ intermetallic compounds. The origin of the main structure of the lines, (namely that each line consists of two components) has been explained in the introduction. We assign the component at

smaller BE. to a transition to the final state with an f -count increased by approximately one compared to the ground state configuration. The relative weight of this component increases with increasing Pd-concentration, both in LaPd_x and CePd_x compounds. We interpret the increase to be due to increased hybridization of the f electrons with the valence electrons /31/.

All spectra were reproducible except the CePd_3 spectrum, which is the most interesting; it has a small peak at 914.7 eV which we attribute to f^0 -like final states. In some cases the f^0 peak was broadened and the f^2 peak less sharp. We tentatively attribute this variation to small quantities of hydrogen in the sample because ~ 1 atomic % hydrogen could be degassed from many samples at high temperatures, and there may have been some surface segregation of the hydrogen. The main sources of hydrogen seem to be the impurities in the initial Ce, cracking of hydrocarbons in the spark erosion process, and hydrogen produced by reaction with atmospheric water. The spectrum shown is that from a sample made with high purity Ce from Ames laboratory and with minimum exposure to air and moisture. We do not have equipment, like SIMS (stimulated ion mass spectroscopy) to monitor the surface hydrogen concentration but it would be interesting to investigate the surface hydrogen concentration as a function of temperature to check if it could explain the anomalous temperature dependance of the XPS spectra /73/.

Figure 14 contains expanded plots of the La and Ce $3d_{5/2}$ peaks from the La-Pd and Ce-Pd intermetallics. Although the f^n and f^{n+1} peaks overlap it is clear that their separation is not constant, but first decreases and then increases with increasing Pd concentration. Note also that the Ce peak widths

are larger than those for La and the peaks broader with increasing Pd content (see also table V).

Plasmon effects, shown in the XPS spectra of LaSn_3 in figure 15, were identified by comparison of the La or Ce and Sn XPS peaks from the compounds in analogy with the method used for CeAl_2 in section IIIa. A plasmon loss of ~ 14 eV is observed on the Sn peaks from the compounds so that plasmon loss satellites of the $3d^9 4f^1$ peaks explain most of the intensity where the $\text{Ce} 3d^9 4f^0$ peaks are normally found in CeSn_3 . We cannot rule out a small $4f^0$ contribution but there is certainly not a large one. The most noticeable feature of the spectra in figure 15 is the very large increase in width of the peaks in LaSn_3 . This makes it difficult to estimate accurately the relative intensity of the f^1 - and f^2 -like peaks in the spectrum accurately, but the f^2 peak intensity seems only a little larger than in Ce metal itself.

d) Compounds with A-group elements: - Au and Al.

The Au compounds were chosen for study because we wish to make separate valence-band studies of the Ce $4f$ levels using synchrotron radiation. The occupied $4f$ levels fall in a region above the main Au $5d$ levels, which have the larger photoionization cross section. In fact even in XPS a contribution of the $4f$ level can be detected at ~ 2 - 2.5 eV in the Au alloys by comparing the spectra of the analogous La and Ce compounds. The $3d$ spectra of LaAu , LaAu_2 , CeAu and CeAu_2 are given in figure 16. The $3d$ peaks are all quite broad so that detection of the f^{n+1} shoulders is difficult, but these are clearly

observed. The shoulders are weak, however, suggesting weak coupling of the 4f levels to the other valence electrons. No XPS peaks corresponding to transitions to f^0 final states were observed.

The 3d spectrum from CeAl_2 , in figure 6, was already discussed in connection with electron energy losses (plasmons) that dominate the regions where " f^0 " peaks are normally found. The f^1 and f^2 peaks are clearly separated, however, and the f^1 peak is nearly as narrow as in Ce itself (see table 5). The relative intensity of the f^2 peak is of the same order as Ce itself (differences are not larger than the accuracy of the deconvolution but in the analogous Th compound XPS lineshape analysis suggests that the f levels are even more decoupled in ThAl_2 than in Th /31/).

e) Ternary compounds

These give the possibility to observe the combined effects of, for instance, A or B and C groups elements on the La and Ce core level lineshapes. Unfortunately the structure of these ternaries is usually not well known. In figure 17 we compare the spectra of CePdAl and LaPdAl . The $3d^9f^n$ peaks are broad although not broader than in some of the binary intermetallic compounds, (table V). It is not possible to say with certainty whether the almost imperceptible f^{n+1} shoulders are stronger or weaker than in the pure elements. We believe that the large linewidths in ternary compounds will be a barrier to lineshape analysis of the combined effects of two different elements on the 4f levels.

IV. DISCUSSION

a) Peak shapes

The main purpose of this section is to discuss the various factors which determine the La and Ce 3d peak shapes in order to allow better assessment of the limitations and strengths of later discussions on the energies and weights of the d^9f^0 , d^9f^1 and d^9f^2 contributions to the spectra. We will also show that the widths of the "poorly screened" core level peaks is a measure of interactions between the f levels of the final state and the valence levels centred on neighbouring sites.

The exchange coupling between the 3d and 4f electrons in lanthanides is smaller than the spin-orbit coupling, but is not negligible /47,49,74-6/ except for the d^9f^0 XPS peaks of La and Ce. This is one reason why these peaks are the narrowest in our XPS spectra, as summarized in table V. We note that the d^9f^0 peak widths can be as low as ~ 1.8 eV, in reasonable agreement with XAS values /47/. However, even in La compounds the d^9f^0 peak is often up to ~ 2.5 eV broader than in the pure metal. Similar broadening is not found in the XAS spectra from the same alloys /77/. As discussed below this broadening contains important information on interactions of f levels in solids but first some spurious explanations must be considered and discarded. It is true that oxidation and contamination does broaden the XPS peaks of lanthanum, but our contamination levels are too low to seriously consider this to be the cause of the large linewidths observed. This was checked by leaving samples in the

instrument for some days to allow contamination to build up to many times the level at which spectra are normally taken: - the effects were observable, but even then they were small by comparison with the differences between La and LaAu for example. In some cases it cannot be ruled out that the large width is due to ambiguity in separation of the well and poorly screened peaks. Indeed it is noticeable that for LaNi_5 and LaPd_3 , where there are strong La $3d^9 4f^1$ contributions overlapping the $3d^9 4f^0$ peaks, the La linewidths given are much larger than for the Ce $3d^9 4f^0$ peaks of CeNi_5 or CePd_3 . However, this explanation does not hold for compounds like LaAu_x or LaPdAl where the contribution of the f^1 peaks are small. We can also reject the explanation that the peak broadening arises from La atoms existing in very different lattice sites because broad La peaks were found in compounds with only one lattice site for the La and because the broadening of the 4d levels is not so significant. A further explanation to be considered is that there is some surface segregation and that regions with different stoichiometry exist near the surface. This explanation we reject on the grounds that the chemical shifts between intermetallic compounds with different stoichiometry (see tables 2,3) are not large enough to explain the peak broadening.

We are thus left with a previously unrecognized contribution to the peak widths. If we had not studied the La compounds we might assumed the changes in linewidths to be a phenomena peculiar to Ce. However, the effects in Ce and La are very similar, as table V shows. We believe the explanation for the broadening lies in the unoccupied 4f level in the poorly screened final state. This is a virtual bound state, and lies about 4-6 eV below E_F in both La and

Ce compounds, as seen from the separation of the f^n and f^{n+1} peaks in tables II and III. This virtual bound state can now interact with the other valence levels in the same energy region so that there is a contribution to its width (and possibly shape) that is related to the strength of the interaction and the density of states near the virtual bound state. The strength of the interaction is a quantity we would dearly like to measure quantitatively, but it would be premature to use more than semi-quantitative arguments at this stage where almost no theoretical back-up is available. Before we get too ambitious we should check the idea that the poorly screened core width comes from the interaction. One test is to look at the density of states in the region of the virtual bound state. ^{If it} ~~If it~~ is small or zero the virtual bound state width, and hence the poorly screened, core level XPS peak width should be smallest. The test works very well. La and Ce, with occupied band widths of 1.5-2 eV and no states 4-6 eV below E_F have the narrowest f^n lines. The LnAu_x alloys, with very large densities of Au d states 4-6 below E_F , have the largest $3d^9 4f^n$ peak widths, and there is even some partially resolved structure in the peaks. LnNi_x and LnPd_x compounds also show $3d^9 4f^n$ peak widths which are larger than in the pure elements, and these also have 3d and 4d, as well as s-bands, extending into the region 4-6 eV below E_F . As shown in table V, the peak widths in CeAl_2 are quite narrow also. Al has a broad band, but quite low density of states. For us, one of the most convincing arguments for the role of the virtual bound state interactions in core-level peak widths in early lanthanides stems from the widths of Ce $3d^9 4f^0$ peaks, where they are observed. These are always narrow, even where the La $3d^9 4f^0$, or Ce $3d^9 4f^1$ peaks are broad, as in LnPd_3 , for example. This is expected in the theory based on interactions of

the unoccupied 4f levels, because the unoccupied $4f^0$ level in Ce final states is 10-15 eV below E_F , where all solid state contributions to its width can be neglected.

We turn now to the d^9f^n multiplet splitting, which is relevant for Ce. Sugar et al. /74,75/ list three $3d^94f^1$ states in XAS due to transitions in La from $3d^{10}4f^0$ ($^1S_0$) atomic like ground states to the $^3P_1$, $3d_1$ and $^1P_1$ states of the $3d^94f^1$ configurations. However, there cannot be just three 3d states for the $3d^94f^1$ configuration in intermediate coupling and we assume that Sugar only listed those states to which an x-ray absorption transition was allowed with the selection rule $\Delta L = \pm 1$, even though we found no explicit comment on this point. In general our Ce 3d XPS peaks are broader and more structureless than the corresponding XAS peaks. We strongly suspect that in XPS the selection rules are less restrictive than in XAS because of the role of the photoemitted electron which can have various symmetries, so that many peaks overlap and can only seldom be resolved. A particularly obvious case is the partially resolved structure ~ 3 eV to the high BE. side of the main Ce $3d^94f^1$ peak, see e.g. figures 4, 9, which has no counterpart in the XAS spectra. The general lesson to be taken from comparison of 3d XPS and XAS spectra with calculations /4,49,75-77/ is that L-S quantum numbers and spin orbit coupling are not adequate in the presence of $3d^94f^n$ interactions. The 3d 4f interactions lead to a broad spread of states around the positions expected in L-S coupling, but most of the states are found within ~ 3 eV of these positions. As this fine structure cannot usually be resolved in XPS we list only a single energy for the $3d^9f^1$ and $3d^9f^2$ peaks in tables II and III.

b) Peak intensities

The individual f^0 , f^1 and f^2 peak intensities give indirect information on the ground state f-counts and also on the f-level hybridization. To extract the relevant peak intensities it is necessary to find some treatment of the background. Here the backgrounds were simply approximated by straight lines joining the intensities at about twice the FWHM on either side of the peaks. This procedure probably underestimates the f^2 peak intensity, as it gives insufficient weight to the high BE f^2 components. The Ce f^0 peak intensities given in table 3 are the $3d_{3/2}$ intensities multiplied by 3/2 to allow for the differences in $3d_{3/2}$ and $3d_{5/2}$ degeneracy. They are larger than the values listed for the 4d f^0 peaks. This is most probably due to difficulties in subtracting a background from the Ce 4f⁰ peaks because these Ce f^0 peaks come in the same region as the energy loss peaks of the complicated Ce 4d⁹4f¹ and 4d⁹4f² XPS peaks.

On inspection of table 3 we see that the ratio of the well-screened: poorly screened ($f^n : f^{n+1}$) peak intensities follow very similar trends in La and Ce compounds, as was previously noted for Ce and Th compounds /31/. As discussed previously, a large shift of weight into the well-screened XPS peaks is indicative of stronger coupling (hybridization) of the screening 4f levels to the other valence electrons /31,51/. We note also that the relative f^0 peak intensity in Ce compounds is largest when the f^2 peak intensity is high, i.e. when the f levels are strongly hybridized with other valence electrons.

We have argued elsewhere that one may not assume that the intensities of f^0 , f^1 and f^2 peaks in core level spectroscopies give directly the weights of f^0 , f^1 and f^2 -like wave functions in the initial state of La and Ce compounds /28,31,32/. We stand by this assertion! Nevertheless it is difficult to believe that the f^0 wave function dominates the ground state of compounds like CeNi₂ or CeNi₅ when there is so little intensity in the

XPS spectrum attributable to transitions to f^0 -like final states. In the sudden approximation we consider the transition probabilities to be controlled by the coefficients found when the initial state is expanded in terms of all the possible final states /57,58/. If, as we argued above, the Ce f^0 -like final state is almost pure f^0 , then we can make the qualitative argument that observation of a f^0 XPS peak indicates an amplitude of f^0 -like wave function in the ground state (for further details see /28/). Model calculations by Schönhammer and Gunnarsson /79/ using experimentally determined parameters support our arguments and indicate that spectra like those of CePd_3 , CeNi_2 and CeNi_5 can be obtained with f -counts of ~ 0.8 , /88,89/ in marked contrast to the ^{traditional} values of 0.0 for the Ni compounds and 0.4-0.6 for CePd_3 /1-3/. In conclusion, it is difficult for us to understand how spectra like ours could be observed if large variations of the ground state f -count in intermetallic alloys did occur. We note also that even for CeO_2 Thornton et al. /41/ calculation partial f -level occupancy, or a covalent contribution for the $4f$ level, and strongly suspect that the "ionic" character of the $4f$ level has been overestimated in the past.

c) $4f$ level widths and hybridization

The calculations of Oh and Doniach /47/, as well as those of Schönhammer and Gunnarsson /79, 88,89/ indicate that a large hybridization potential, V_{vf} , is necessary to explain the observed spectra for compounds like CePd_3 , CeNi_2 and CeNi_5 . The values obtained range from ~ 0.5 to 1.5 eV depending on the exact treatment of degeneracy in the initial and final states. This gives an f -level width of $V_{vf} \sim 0.3$ eV. This width could have two origins : f - f

overlap as in the Mott-transition model for Ce and hybridization with s-d states or states of the partner element. We may immediately rule out effects of f-f overlap, because the increase in the well-screened peak intensities with increasing Ni or Pd content in La or Ce alloys indicates increased hybridization despite an increase in the average La-La or Ce-Ce distance. This distance is almost a factor of two larger in LaNi_5 or LaPd_3 than the pure element, and as the f-f overlap decreases with the third to fifth power of the distance between the atoms /80,81/ it is negligible in these compounds. We thus find that the only models at present available to interpret our data indicate 4f hybridization with other valence orbitals to a degree not previously envisaged.

d) Comparison with other measurements

All experimental methods yielding information on f-counts and widths involve complexities and uncertainties comparable to photoemission. Nevertheless the role of the 4f levels in La and Ce will never be understood unless we try to explain why different methods yield such conflicting results. The explanation must lie in the differences in what different techniques measure. We start by comparing the trends in f-level hybridization found by us with conventional ideas about f count in Ce compounds derived from lattice constant and magnetic measurements. These ideas were summarized with the help of figure 1, which was adapted from /3/. The conventional idea was that in compounds with elements in region A, Ce had f-count below 1, i.e. a valence greater than 3, and for a-richest compositions tetravalent Ce (f-count=0) would be found. It was also thought that B elements formed compounds with Ce in intermediate valence states (f-count between 0 and 1) and with C-elements the valency of Ce would be 3

/1-7/.

Our interpretation of the XPS results presented here is not in agreement with these conventional ideas. We find that for a given stoichiometry the 4f hybridization for A-compound . B-compounds . C-compounds, but the indication is that the f-count does not change very much. Interestingly enough, the intensity of the f^0 peaks is greatest in the A-richest compounds, such as $CeNi_5$ and $CeNi_2$ (this work) $CeRu_2$ /82/, $CeCo_5$ and $CeRh_3$ /36/. The f^0 peaks are also found in some of the so-called mixed valence materials such as δ -Ce, /67/, $CePd_3$ (this work) and CeN , /68/, but not in compounds with C-elements such as $CeAu_2$ or $CeAl_2$. We have argued elsewhere /28/ that observation of f^0 peaks in XPS is an indication of some f^0 character in the ground state, but is not a reliable indication of its quantity. However, as stated above that we have no explanation for the small sizes of the f^0 peaks found if there are large amplitudes of f^0 character in the ground state (we envisage a maximum of 5-30%). This conclusion is in agreement with Compton scattering measurements on ~~ce~~Ce /15/ and thermodynamic arguments for Ce /12-14/ and its compounds. It implies that f-counts derived from lattice constants or magnetism have taken insufficient account of the coupling of the f electrons to the other valence electrons. In our interpretation of the spectra this coupling is largest in Ce compounds with A-elements and, interestingly, smaller in compounds with B and C-elements. We propose that this coupling, or hybridization is correlated with changes in lattice constant, and suggest that one should consider the possible mechanisms by which such effects could arise. We consider the observation of Ce $3d^9 4f^0$ XPS peaks to be an indication of a small amount of "band character" in the Ce 4f levels rather than as a firm

indication of "mixed valence". The $3d^9 4f^0$ peaks are principally although not completely diagnostic of an initial state effect, not a final state effects.

Our conclusion that the f-count is nearly constant in Ce and its intermetallic is not necessarily inconsistent with a fairly sharp f level moving through the Fermi level as the chemical composition is changed and as suggested by some valence band photoemission /24,83/ and Bremsstrahlung isochromat spectroscopy (BIS) /24,25/ results. A possible idea which would reconcile the two concepts is illustrated in figure 18. First we illustrate the f level in the promotional model as a single peak which can move through the Fermi level according to chemical environment. (Note that the normalization of this curve as it moves through E_F is not as trivial as we have shown because in the lower figure there is only one way to remove an electron but in the top figure the area can be normalized to 14 as there are 14 ways of adding an electron, even though only one electron at a time may be added because of correlation effects. The second set of drawings illustrates schematically the effect of width changes, as in the Mott-transition model. In the model we wish to consider we give added importance to the other states of the system, for instance, the Ni d states in $CeNi_x$. As the hopping integral between f and other orbitals increases the 4f level widens and some Ce-f character is found in the bands with predominantly partner element character (e.g. Ni 3d or Pd 4d). This character would (at least partially) compensate for the loss of f-character from the emptying of the nearly sharp f-level as it is pushed above E_F . Indeed one could conceive of this f character in the partner band causing the shift of the sharp f level. If the f-count associated with the f character in the partner band is ρ and the effective f-f Coulomb integral is U_{eff} then the electron

affinity of the nearly sharp and pure f level is decreased by approximately ρU_{eff} with respect to that in the case where there is no hybridization with the partner band.

More experiments with BIS and photoemission spectroscopy in Fano resonance are needed to test the ideas illustrated in figure 18. However, it is not unreasonable to suggest some form of interatomic "hybridization". Amongst others, Wittig suggested the need to incorporate such effects for light lanthanides ten years ago /16/. Effect like those in figure 18 also have analogies in the non-Lorentzian shapes calculated for $3d$ resonances of transition metals dissolved in simple, or noble metals /84/ as well as in the mixing of bands formed from states with different energies for the effective atomic energy (see e.g. ref. 65 and references therein). We stress that the model suggested in figure 18 cannot be much more than a framework within which detailed calculations could be made and that it could be used in conjunction with Schluter-Varma double-wells /21/ or Kondo-like effects /17-20/, heavy phonon effects, etc.

e) Possible determination of the Ce $4f$ level position by core level spectroscopy.

It has been argued that a core ionized La atom resembles a Ce atom in an La matrix, and that this may be used to determine the $4f$ binding energies in Ce compounds /85/. It is assumed that a La matrix has similar properties to those of a "trivalent" Ce matrix and that the difference in the La $3d^{9f^1}$ and $3d^{9f^0}$ binding energies corresponds closely to the energy required to

make the transition $\text{Ce } 3d^{10}f^1 \rightarrow 3d^{10}f^0$. When applied to the atomic elements and compared with calculations it was found that the use of the Z+1 approximation overestimated the 4f binding energy by 2.1 eV. It is educational to consider the case of δ -Ce. Here there has been some controversy about whether the 4f level was ~ 1.8 or ~ 0.2 eV /24/ below E_F . The value calculated from the Z+1 approximation would be $(f^1 - f^0) \text{ La} - 2.1 \text{ eV} = 3.2 - 2.1 = 1.1 \text{ eV}$. The authors of reference /85/ has a vested interest in the 1.8 eV position for the 4f level in δ -Ce /12,13/ and argued that 1.1 eV was in reasonably good agreement with 1.8 eV considering the experimental accuracy. This was true, but there is now a strong suggestion that two 4f-derived peaks can be seen in the photoemission spectra of Ce at ~ 1.8 and $\sim 0.0-0.2$ eV /86/ so that the value from core level spectroscopy and the Z+1 approximation is near the centroid of both.

We believe that the use of the Z+1 approximation for this question shows some promise, but the case of δ -Ce shows up some of the uncertainties involved. Other uncertainties involve the multiplet splitting due to 3d-4f interactions. The one point that we would make is that $\delta(f - f^0)$ is generally larger in the La intermetallics where mixed valence and tetravalent Ce was formerly postulated in the Ce analogues. This would imply a larger binding energy for the 4f centroid in these Ce compounds. The combination of the Z+1 approximation and core level XPS of La intermetallics thus provides no evidence for a description of Ce intermetallics involving large changes in f-count. However, a complete analysis of this problem must include the interactions of the 4f virtual bound states described in section IVa. It must be recognized that such interactions can strongly shift the final state f^n level as well as broaden it, and such

shifts make the approximation invalid.

V. CONCLUDING REMARKS

This paper concentrated on the use of the 3d core level lineshapes in XPS as a diagnostic tool for the properties of the La and Ce 4f level. The spectra show contributions arising from transitions to f^0 -, f^1 - and f^2 -like final states whose weight does not give directly the weight of the f^0 , f^1 and f^2 wave functions in the ground state. However, it is not possible for us to rationalize the observed spectra in terms of large changes in 4f-count, as have been postulated in the past. Using ideas on the connection between screening level hybridization and core level lineshapes [31] we deduce that the Ce 4f levels are most strongly coupled to (hybridized with) the other valence electrons in compound that have sometimes been called mixed valent, and f^0 materials. Studies of LnNi_x and LnPd_x alloys as a function of stoichiometry indicated that the effects of hybridization increase despite increasing Ln-Ln separation and must thus be attributed to hybridization between the 4f levels and orbitals centred on the other sites (Ni-d, Pd-d, etc.). We have suggested a model for the 4f distribution in the valence band in which incorporation of 4f character into the "partner" bands leads to shifts in the narrow 4f bands due to electron correlation effects.

Whilst we have a qualitative, and sometimes semi-quantitative understanding of screening and hybridization effects on core level XPS of La and Ce compounds, there are other aspects of the spectra which are poorly understood. These include the variation in measured linewidths and the chemical shifts of the various components of the XPS lines. It is thought that at least part of these

problems arise from the nearly localized nature of the 4f levels in the early lanthanides and that if these features were better understood we would have more insight in to the nature of the 4f levels themselves. An important clue to the interactions in the ground state is given by the observation of strong broadening of the poorly screened (f^n) peaks when the virtual bound state that is the screening level lies in the partner element d bands. This broadening is weaker in Ni alloys where the 4f virtual bound state lies at the bottom, or below the Ni d bands, and materials like Ce or CeAl_2 where there are no such bands. In LnSn_3 the 4f virtual bound states lie in the Sn 5s-5p bands and the broadening is intermediate between, say, LnAu_x and CeAl_2 . This suggests that the strength of interaction between 4f and Sn 5s-5p bands is intermediate between the strengths of 4f-nd and 4f-Alsp interactions. Using this information and the knowledge that the "natural" or effective atomic 4f level is 0-2 eV below E_F we can propose a rationalization of the characteristics shown by Ce compounds with A-, B- and C- elements. The A-group elements are transition metals d where the 4f level always lies in the transition metal d band and is strongly hybridized with these bands in Ce-TM compounds. The Pd 4d and Pt 5d bands are readily filled and pushed some way below E_F in compounds with Ce so that it is only in Pd or Pt-rich compounds that Pd or Pt d states reach to E_F /65/ and the Ce 4f-Pd/Pt d hybridization has its full effect. In compounds with Cu, Ag and Au, as well as other C group elements the high density of d states is well below E_F , or, as in Mg and Al, they are not present at all. As we move across the periodic table to the right the interaction between the Ce 4f level and the other levels must become stronger again, perhaps just because the density of partner element states within ~ 2 eV of E_F increases as the number of electrons/ partner element increases.

There are several experimental lines of investigation which could be used to extend the systematics proposal here. For instance XPS investigation of $\text{CePd}_x\text{Ag}_{3-x}$, or CeNi_xCu_y or CePt_xAu_y ternaries, where the density of transition metal d states near E_F can be varied. Bremsstrahlung Isochromat studies would also give information on the unoccupied 4f states. However, neither of these lines of research would necessarily give more decisive evidence on whether the promotional model (Fig. 18a) or the model described by figure 18c is a more appropriate description of the Ce 4f level behaviour. Both models have a more or less sharp 4f level moving through E_F . However, it is to be hoped that an increased data base from electron and x-ray spectroscopies will yield results that are more tractable for theoretical methods.

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Table I

Electron energy loss features in ELS spectra of La and Ce
(all values in eV, error limits in parenthesis)

Loss	La	Ce
a	3.0 (0.2)	3.2 (0.2)
b	5.8 (0.4)	---
c	7.8 (0.2)	8.0 (0.2)
d	12.4 (0.5)	12.0 (0.5)
e	19.4 (0.8)	19.3 (0.8)
g	28.2 (0.5)	29.4 (0.5)

Table II

3d XPS peak binding energies for La intermetallic compounds

(all values in eV with respect to E_F)

	$3d_{3/2}$				$3d_{5/2}$				Δ^*	$\delta_{3/2}$	$\delta_{5/2}$
	f^0	$\pm$	f^1	$\pm$	f^0	$\pm$	f^1	$\pm$	S.O. f^0-f^1	f^0-f^1	f^0-f^1
La	852.6	0.2	848.85	0.6	835.8	0.2	832.9	0.6	16.8	3.7	3.1
La	852.2	-	848.7	-	835.4	-	832.0	-	16.8	3.5	3.4
La	—	-	—	-	835.6	-	832.4	-	—	-	3.2
La ₃ Ni	852.8	0.2	849.4	0.5	835.9	0.2	832.6	0.5	16.9	3.4	3.3
La ₇ Ni ₃	—	-	—	-	835.8	0.2	832.3	0.4	—	-	3.5
LaNi	—	-	849.7	0.6	836.2	0.3	832.7	0.6	—	-	3.5
LaNi ₅	—	-	848.6	0.6	835.9	0.3	832.1	0.5	—	-	3.8
La ₇ Pd ₃	852.9	0.3	849.0	0.6	836.0	0.3	832.2	0.5	16.9	3.9	3.8
LaPd	853.7	0.3	851.1	0.6	836.8	0.3	834.3	0.6	16.9	2.6	2.5
LaPd ₂	854.0	0.3	851.2	0.6	837.0	0.3	834.3	0.5	17.0	2.8	3.3
LaPd ₃	854.0	0.2	849.8	0.4	837.0	0.2	832.9	0.4	17.0	4.2	4.1
LaSn ₃	853.1	0.3	848.8	0.6	836.4	0.3	831.8	0.5	16.7	4.3	4.6
LaAu	853.3	0.5	—	-	836.4	0.5	832.1	1.0	16.9	-	4.3
LaAu ₂	852.8	0.3	—	-	836.0	0.3	832.2	1.0	16.8	-	3.8
LaPdAl	853.1	0.2	848.6	0.8	836.3	0.2	831.8	0.8	16.8	4.5	4.5
LaH ₃	855.5	-	851.8	-	838.7	-	835.0	-	16.8	3.7	3.7
La ₂ O ₃ ^a	855.8	-	851.3	-	839.0	-	834.5	-	16.8	4.5	4.5

 Δ^* spin orbit splitting

a = ref. 42

b = ref. 34

c = ref. 39

Table III 3d XPS binding energies for Ce intermetallic compounds
(all values in eV with respect to E_F)

	$3d_{3/2}$						$3d_{5/2}$						As.o. $\delta f^0 - f^1$ $\delta f^1 - f^2$		
	f^0	$\pm$	f^1	$\pm$	f^2	$\pm$	f^0	$\pm$	f^1	$\pm$	f^2	$\pm$			
Ce	---	-	901.7	0.3	896.4	1.0	---	-	883.7	0.2	878.5	0.5	18.0	--	5.2
Ce ^a	---	-	901.8	0.3	---	-	---	-	883.2	-	879.3	-	18.6	--	3.9
Ce ^b	---	-	---	-	---	-	---	-	883.7	-	878.8	-	-	--	4.9
CeCo ₂	913.8	0.3	902.9	0.3	897.0	0.8	895.4	0.6	884.4	0.3	878.9	0.6	18.5	10.9	5.5
CeCo ₅	914.1	0.6	902.8	0.6	897.8	1.0	895.4	1.0	884.4	0.6	879.3	0.9	18.4	11.1	5.1
Ce ₇ Ni ₃	---	-	902.3	0.2	896.8	0.5	---	-	883.9	0.2	878.6	0.5	18.4	--	5.3
CeNi	913.8	0.3	902.4	0.2	896.3	0.5	---	-	884.0	0.2	878.5	0.4	18.4	11.4	5.5
CeNi ₂	914.0	0.3	903.0	0.2	897.4	0.5	895.6	0.5	884.5	0.2	878.8	0.4	18.5	11.0	5.7
CeNi ₅	913.9	0.3	903.1	0.3	898	2.0	895.8	0.5	884.6	0.3	878.9	0.4	18.5	10.8	5.7
CeRu ₂	914.0	0.3	903.2	0.3	896.1	1.0	895.7	1.0	884.8	0.3	878.9	0.7	18.4	10.8	5.9
Ce ₇ Pd ₃	---	-	902.7	0.2	896.6	2.0	---	-	884.2	0.2	878.2	0.8	18.5	--	6.0
CePd	---	-	903.1	0.2	898.8	0.6	---	-	884.6	0.2	879.8	0.7	18.5	--	4.8
Ce ₃ Pd ₅	---	-	903.0	0.2	898.7	0.5	---	-	884.6	0.2	879.9	0.5	18.4	--	4.7
CePd ₃	914.7	0.3	902.9	0.2	898.5	0.5	---	-	884.3	0.2	879.6	0.5	18.6	11.8	4.7
CeSn ₃	---	-	902.9	0.3	---	-	---	-	884.6	0.2	878.0	0.6	18.3	--	6.6
CePt ₃	915.1	0.4	903.4	0.4	899.3	1.0	897.0	0.8	885.0	0.4	879.7	0.9	18.4	11.8	5.3
CeAu	---	-	903.0	0.3	896.4	0.8	---	-	884.4	0.3	877.7	0.8	18.6	--	6.7
CeAu ₂	---	-	903.2	0.4	---	-	---	-	884.7	0.4	878.1	1.0	18.5	--	6.6
CeAl ₂	---	-	901.9	0.4	---	-	---	-	883.5	0.4	877.8	-	18.4	--	5.7
CePdAl	---	-	902.5	0.4	896.5	1.0	---	-	884.0	0.3	878.0	0.8	18.5	--	6.0
CeCu ₂ Si ₂ ^c	---	-	902.1	0.4	897.3	0.8	---	-	883.6	0.4	878.8	0.6	18.5	--	4.8
CeSe ^c	---	-	903.9	0.4	899.6	0.8	---	-	885.3	0.4	879.8	0.4	18.6	--	5.5

Table III Cont.

CeSb ^c	---	902.8	-	---	-	---	-	884.6	-	---	-	18.2	---	-
Ce ₂ O ₃ ^a	---	904.5	-	899.9	-	---	-	886.1	-	881.3	-	18.4	---	4.8
CeO ₂ ^a	916.7	907.3	-	900.2	-	898.2	-	888.4	-	882.4	-	18.9	9.4	6.2
CeH _{2.1} ^d	---	904.0	-	~900	-	---	-	885.7	-	~882	-	18.3	---	~4
CeH _{2.9} ^d	---	904.2	-	~900	-	---	-	885.9	-	~882	-	18.3	---	~4

a = ref. 42 .

b = ref. 34

c = ref. 30

d = ref. 40

Table IV

Relative intensities of peaks due to f^0 , f^1 and f^2 final states in La3d, Ce3d and Ce4d XPS spectra (all values normalized to give total intensity = 1.0; comparisons between compounds are reliable to 10%, absolute values depend on deconvolution procedure).

Compound	La3d $f^0:f^1$	Ce3d $f^0:f^1:f^2$	Ce4d $f^0:f^1+f^2$
R	0.83:0.17	<0.04:0.92:0.08	0:1.0
R ^a	0.83:0.17	<0.04:0.89:0.11	---
α Ce ^b	---		<0.03:0.97
CeCo ₂		0.10:0.65:0.25	---
CeCo ₅	---	0.07:0.70:0.23	---
R ₃ Ni	0.82:0.18	---	---
R ₇ Ni ₃	0.8 :0.20	<0.04:0.85:0.15	<0.03:1.0
RNi	0.74:0.26	0.02:0.82:0.16	0.03:0.97
RNi ₂	---	0.06:0.72:0.22	0.05:0.95
RNi ₅	0.69:0.31	0.12:0.72:0.17	0.06:0.94
R ₇ Pd ₃	0.88:0.12	<0.04:0.93:0.07	<0.03:1.0
RPd	0.71:0.29	<0.04:0.80:0.20	<0.03:1.0
Ce ₃ Pd ₅	---	<0.04:0.74:0.26	<0.03:1.0
LaPd ₂	0.69:0.31	---	---
RPd ₃	0.58:0.42	0.05:0.65:0.30	~ 0.04:0.96
CeRu ₂ ^c	---	0.12:0.61:0.27	~ 0.06:0.93
CeRh ₃	---	~ 0.16:0.53:0.32	~ 0.07:0.93
RSn ₃	0.83:0.17	< 0.06:0.94:0.06	<0.06 :1.0
CePt ₃	---	<0.07:0.64:0.29	---
RAu	0.92:0.08	<0.04:0.94:0.06	<0.03:1.0
RAu ₂	0.93:0.07	<0.04:0.97:0.03	<0.03:1.0
RAl ₂	---	<0.10:0.93:0.07	<0.10:1.0
RPdAl	0.38:0.17	<0.10:0.91:0.09	<0.03:1.0
CeCu ₂ Si ₂ ^d	---	0.04:0.91:0.09	<0.03:1.0
CeN	---	~ 0.12:0.59:0.29	~ 0.09:0.91
CeSb ^d	---	<0.05:0.83:0.17	<0.05:1.0
CeSe ^e	---	<0.04:0.71:0.29	<0.03:1.0
R ₂ O ₃	0.42:0.58	<0.10:0.56:0.44	---
CeO ₂ ^a	---	~ 0.25:0.18:0.56	---
RH ₂ ^f	---	<0.10:0.80:0.20	---
RH ₃ ^f	~0.71:0.29	<0.10:0.80:0.20	---

a = ref. 42, b = ref. 67, c = ref. 36, d = ref. 68, e = ref. 30, f = ref. 40

Table V

Full widths at half maximum for the La and Ce $3d_{5/2}$ peaks
(all values in eV, $\pm 10\%$)

Compound	La f^0	Ce f^1	Ce f^0 $3d_{3/2}$	f^n
R	1.8	2.8	-	
R ₃ Ni	2.1	-	-	
R ₇ Ni ₃	2.2	3.8	-	
RNi	2.3	3.8	-2	
RNi ₂	-	4.6	2.0	
RNi ₅	3.1	4.3	1.7	
R ₇ Pd ₃	3.0	3.4	-	
RPd	3.0	3.8	-	
Ce ₃ Pd ₅	-	4.0	-	
LaPd ₂	3.5	-	-	
RPd ₃	2.8	4.1	1.7	
RSn ₃	2.2	4.7	-	
RAu	-4.0	4.8	-	
RAu ₂	-4.5	6.0	-	
RAl ₂	-	3.0	-	
RPdAl	3.5	4.1	-	
PrPd ₃	-	-	-	4.6
NdPd ₃	-	-	-	3.8

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FIGURE CAPTIONS

- FIG. 1: Conventionally accepted categories of Ce compounds, for explanation see text. We will show below that such a scheme is not helpful in the interpretation of XPS results, and may be wrong.
- FIG. 2: Schematic diagram of excitation of a 3d core hole in XPS of La and Ce compounds. The excitation takes place from an initial state into final states whose approximate configurations are $3d^9 4f^0$, $3d^9 4f^1$ and $3d^9 4f^2$.
- FIG. 3: Illustration of the peak assignments for the XPS spectrum of Ce in the region of the Ce 3d peaks. The peaks are labelled according to their approximate final state configuration - i.e. the f counts are not necessarily exactly integral. In the following diagrams the final states are labelled f^0 , f^1 , and f^2 , and the 3d hole is not mentioned specifically.
- FIG. 4: 3d core level XPS and electron energy loss ELS spectra for La and Ce. The ELS spectra have been normalized so that the area of the primary peaks are equal to the areas of the main La or Ce $3d_{5/2}$ XPS peaks.
- FIG. 5: Top: XPS spectra in the region of the Al 2p and 2s and Ce 4d XPS spectra from $CeAl_2$.
Bottom: Same spectra after subtraction of plasmons.

FIG. 6: Ce 3d XPS spectrum from CeAl_2 with plasmon losses labelled.

FIG. 7: Comparison of the La XPS spectrum in the La 3d peaks, as excited by AlK α radiation, with the x-ray excited Auger spectrum in the same kinetic energy region.

FIG. 8: La 3d and Ni 2p XPS spectra from La-Ni alloys

FIG. 9: Ce 3d XPS spectra from Ce-Ni alloys

FIG. 10: Ce 4d XPS spectra from Ce-Ni alloys

FIG. 11: La $3d_{5/2}$ and Ce $3d_{5/2}$ peaks from La-Pd and Ce-Pd alloys

FIG. 12: La 3d XPS spectra from La-Pd alloys

FIG. 13: Ce 3d XPS spectra from Ce-Pd alloys

FIG. 14: La $3d_{5/2}$ and Ce $3d_{5/2}$ peaks from La-Pd and Ce-Pd alloys

FIG. 15: 3d XPS spectra from LaSn_3 and CeSn_3 alloys

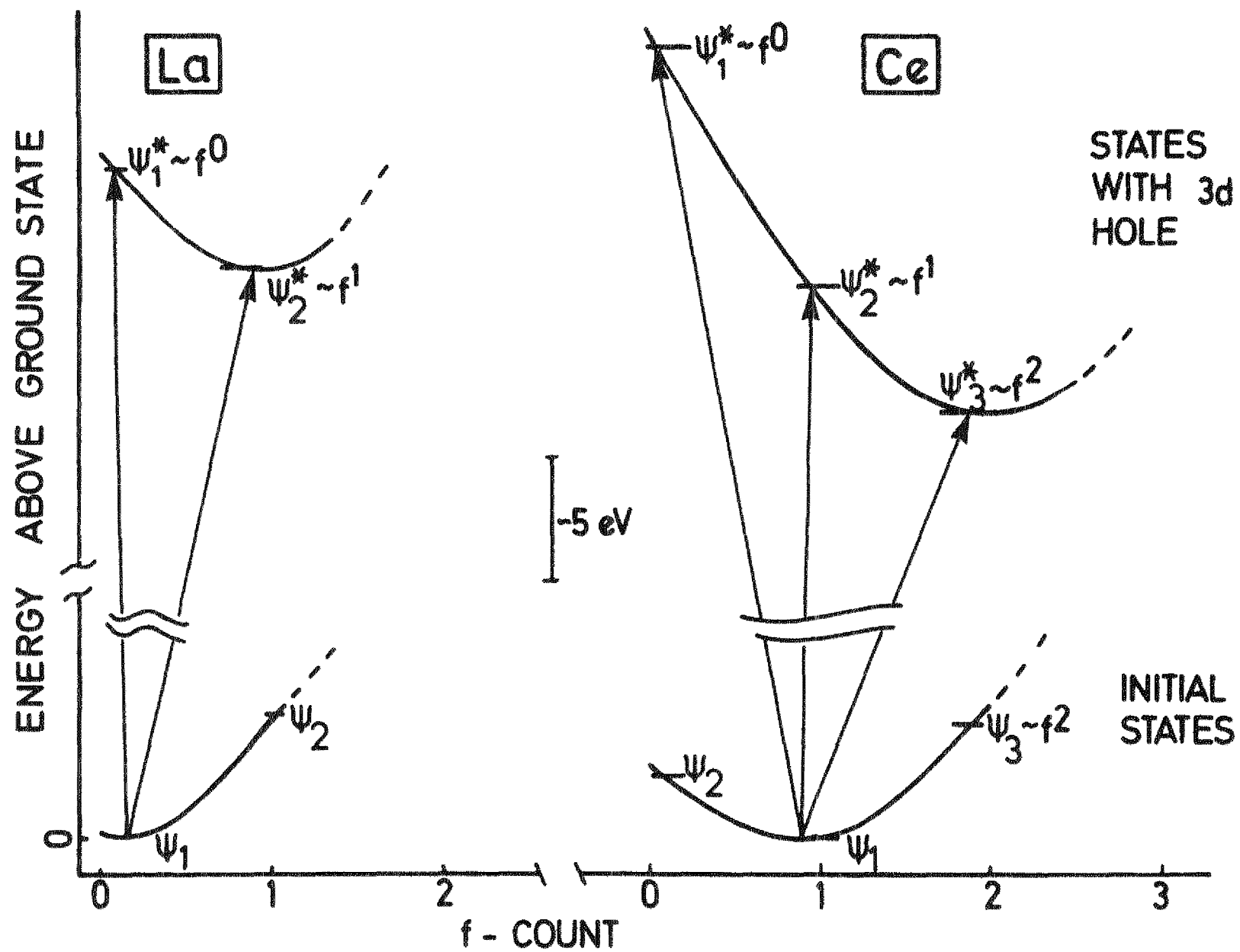
FIG. 16: 3d XPS spectra from La-Au and Ce-Au alloys

FIG. 17: 3d XPS spectra from LaPdAl and CePdAl

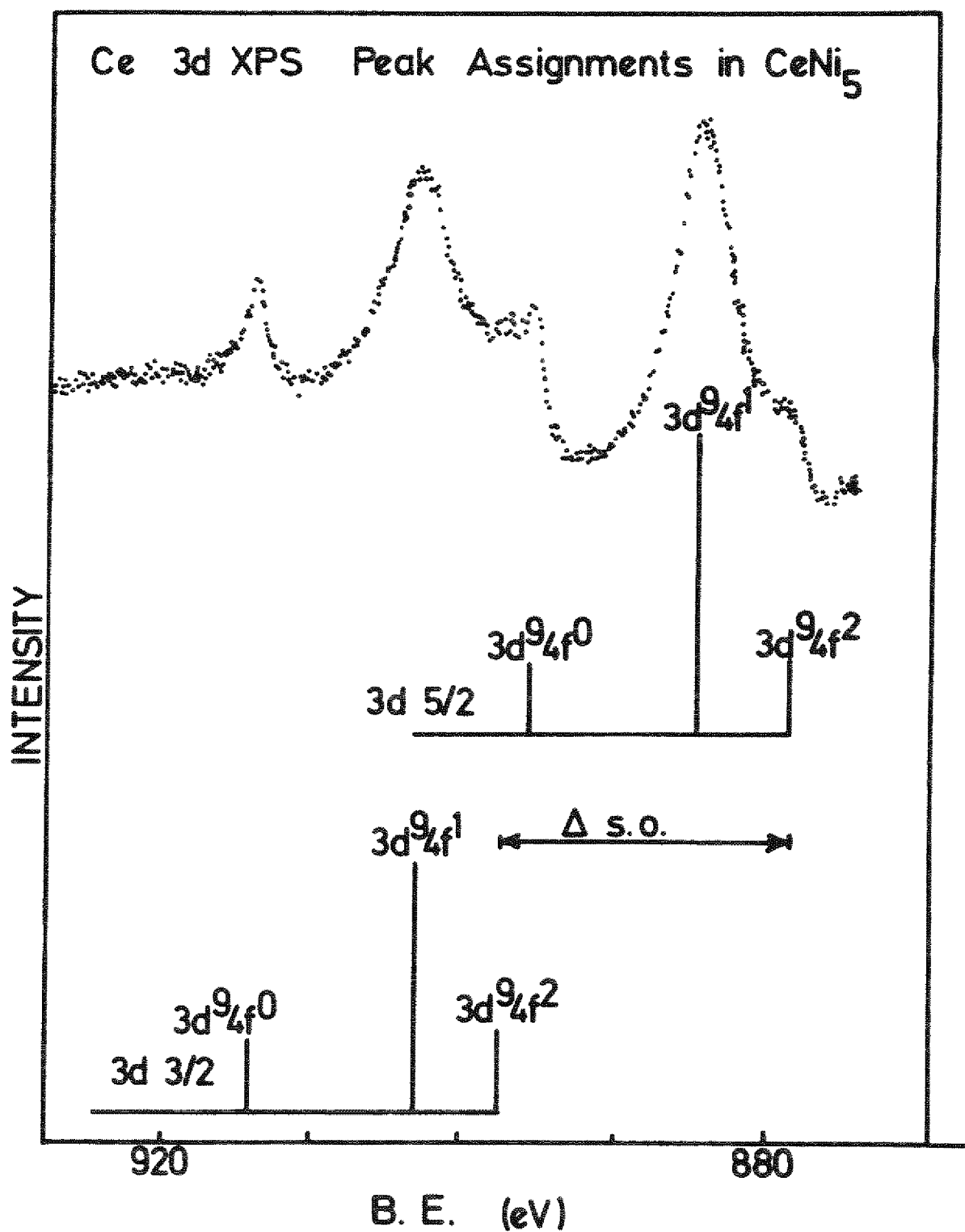
FIG. 18: Models for 4f character distribution in Ce and its alloys. - Ce4f states; partner states. Note that the intensity ratios of "band-like" and "localized" 4f character is not drawn to scale. The BE increases from right to left on the x axis and the DOS is the y axis.

A				B			
Os	Ir	Pt	Au	Hg	Tl	Pb	Bi
Ru	Rh	Pd	Ag	Cd	In	Sn	Sb
Fe	Co	Ni	Cu	Zn	Ga	Ge	As
				Mg	Al	Si	P
				Be	B	C	N
A				B			
C				B			
B				C			

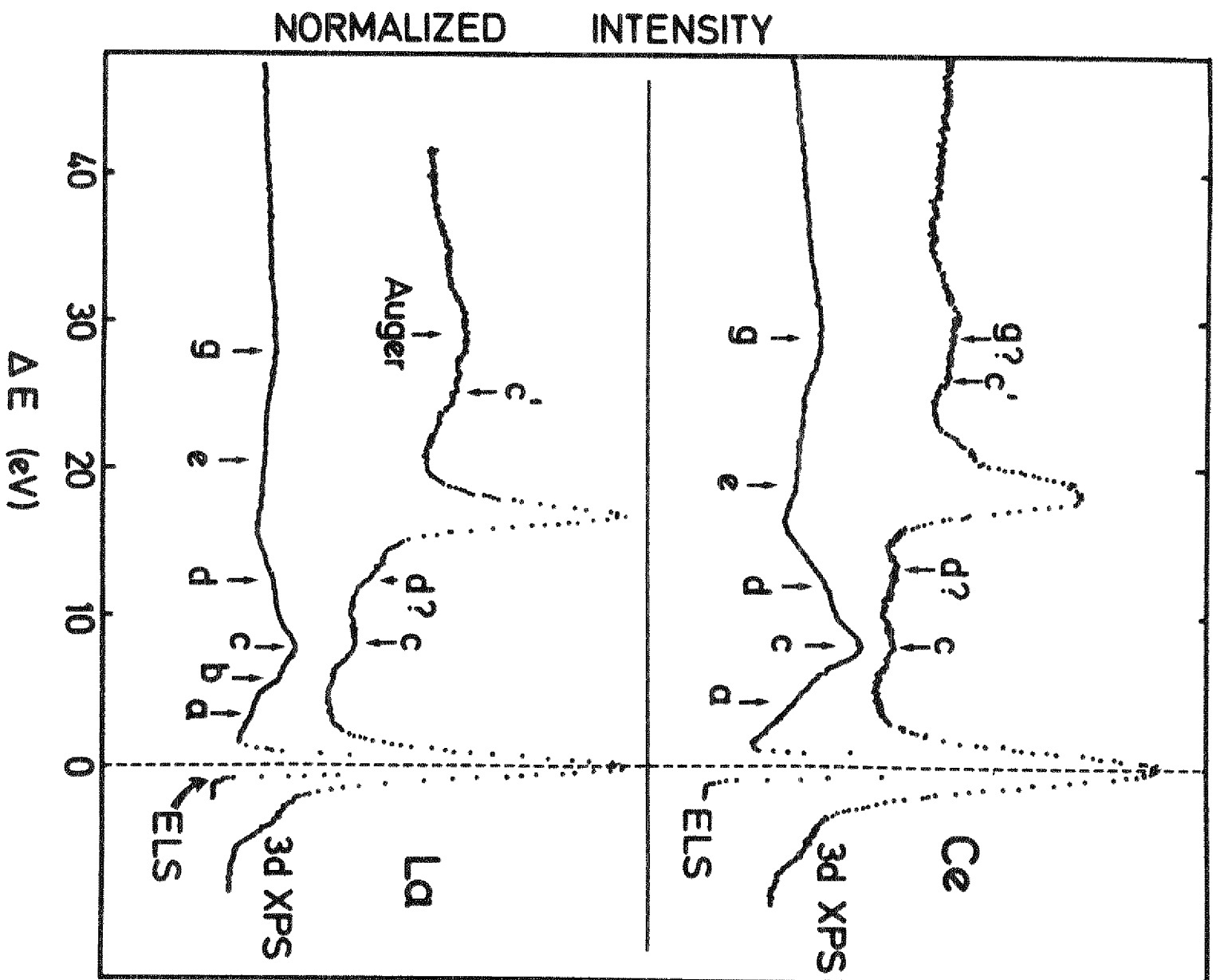
Fuggle et al
Fig. 1



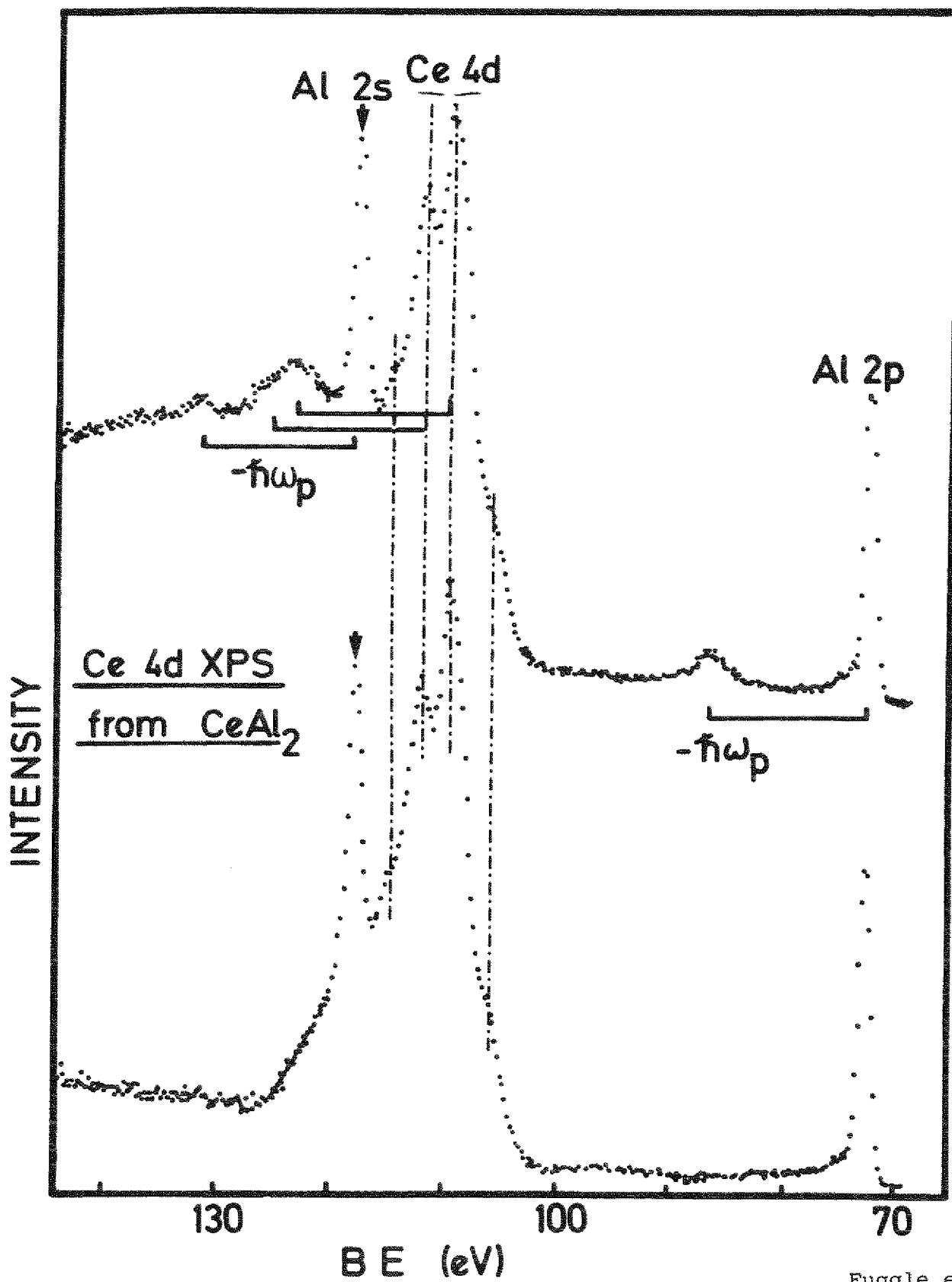
Fuggle et al
Fig. 2



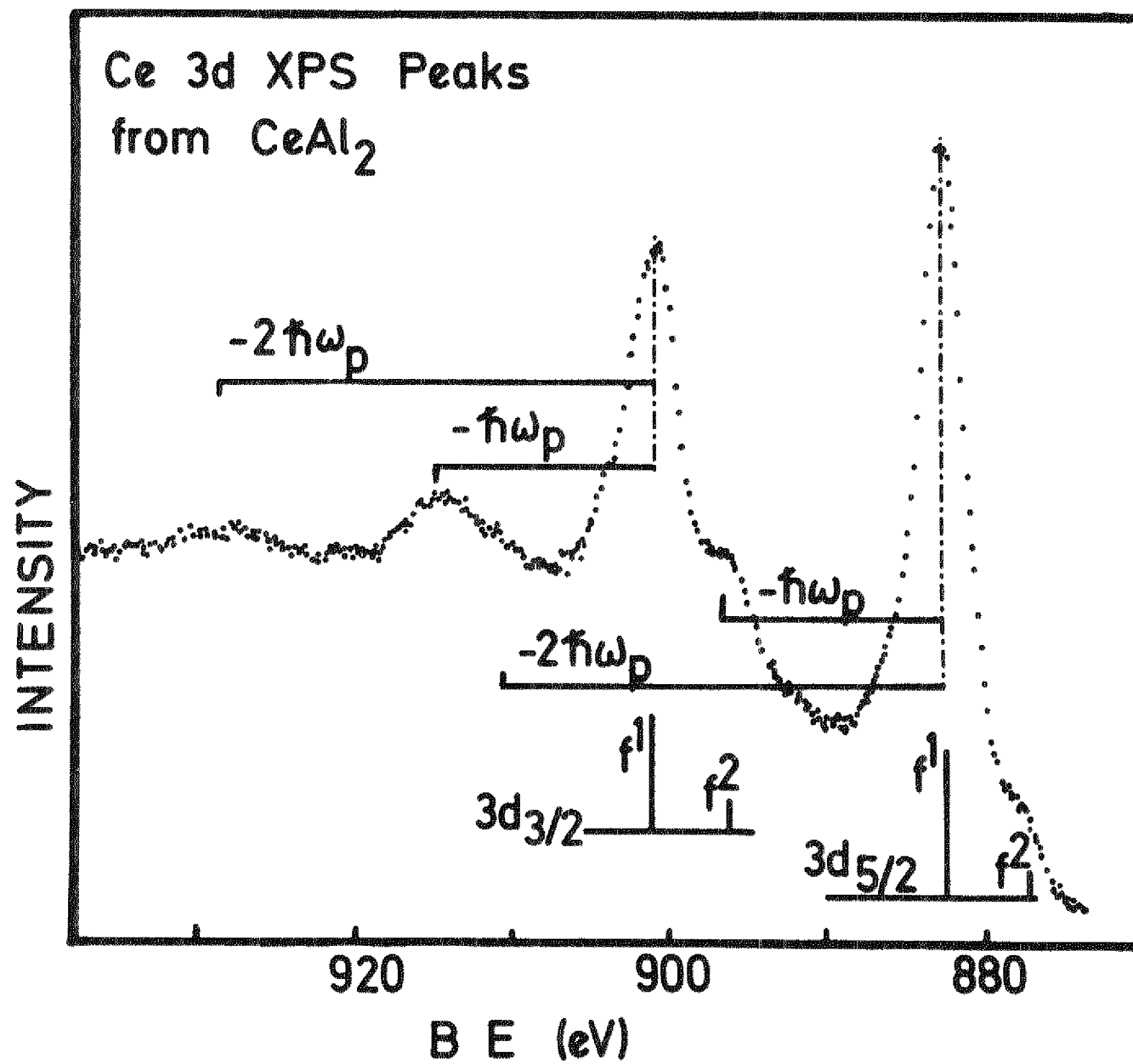
Fuggle et al
Fig. 3



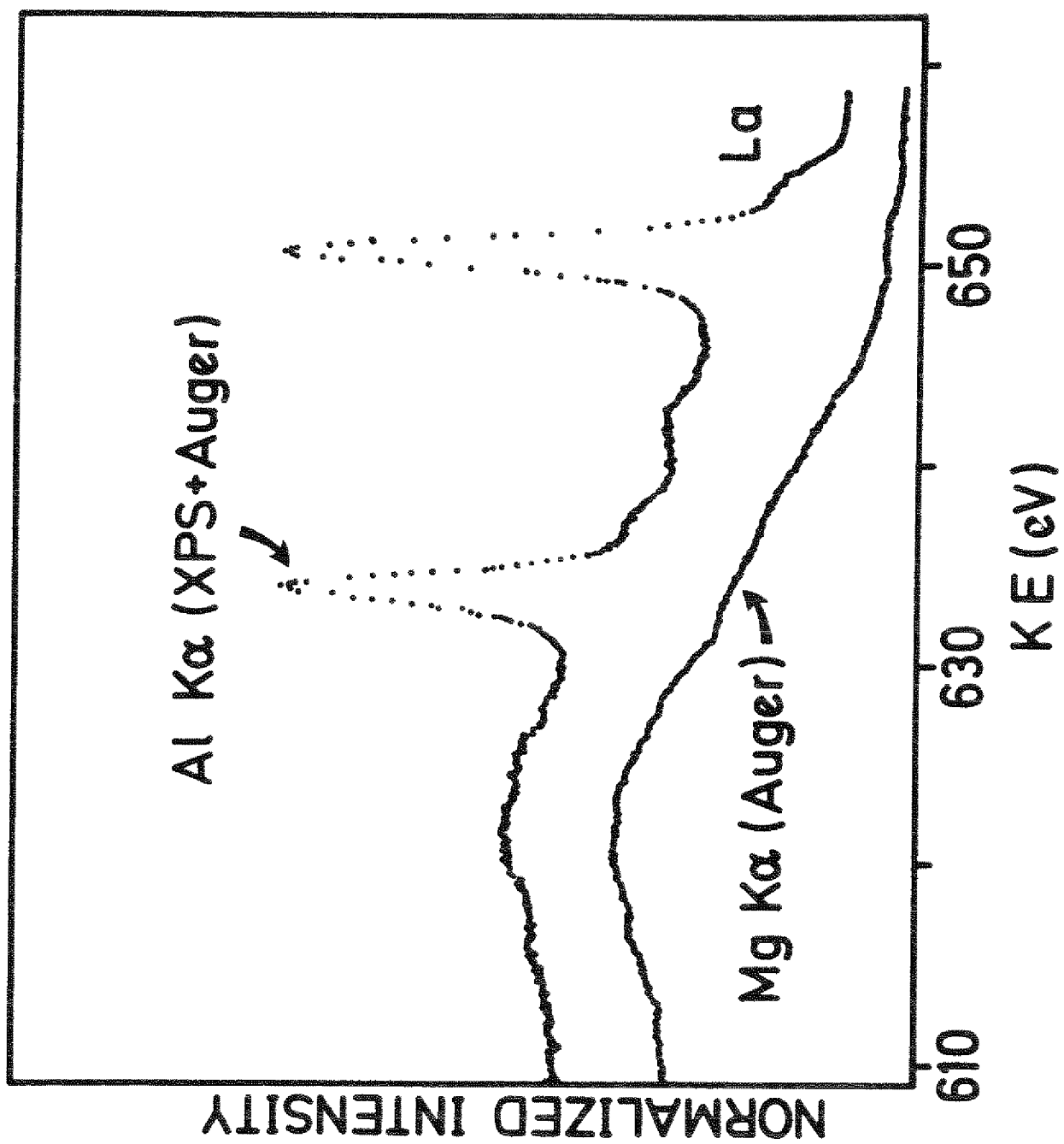
Fuggle et al
Fig. 4



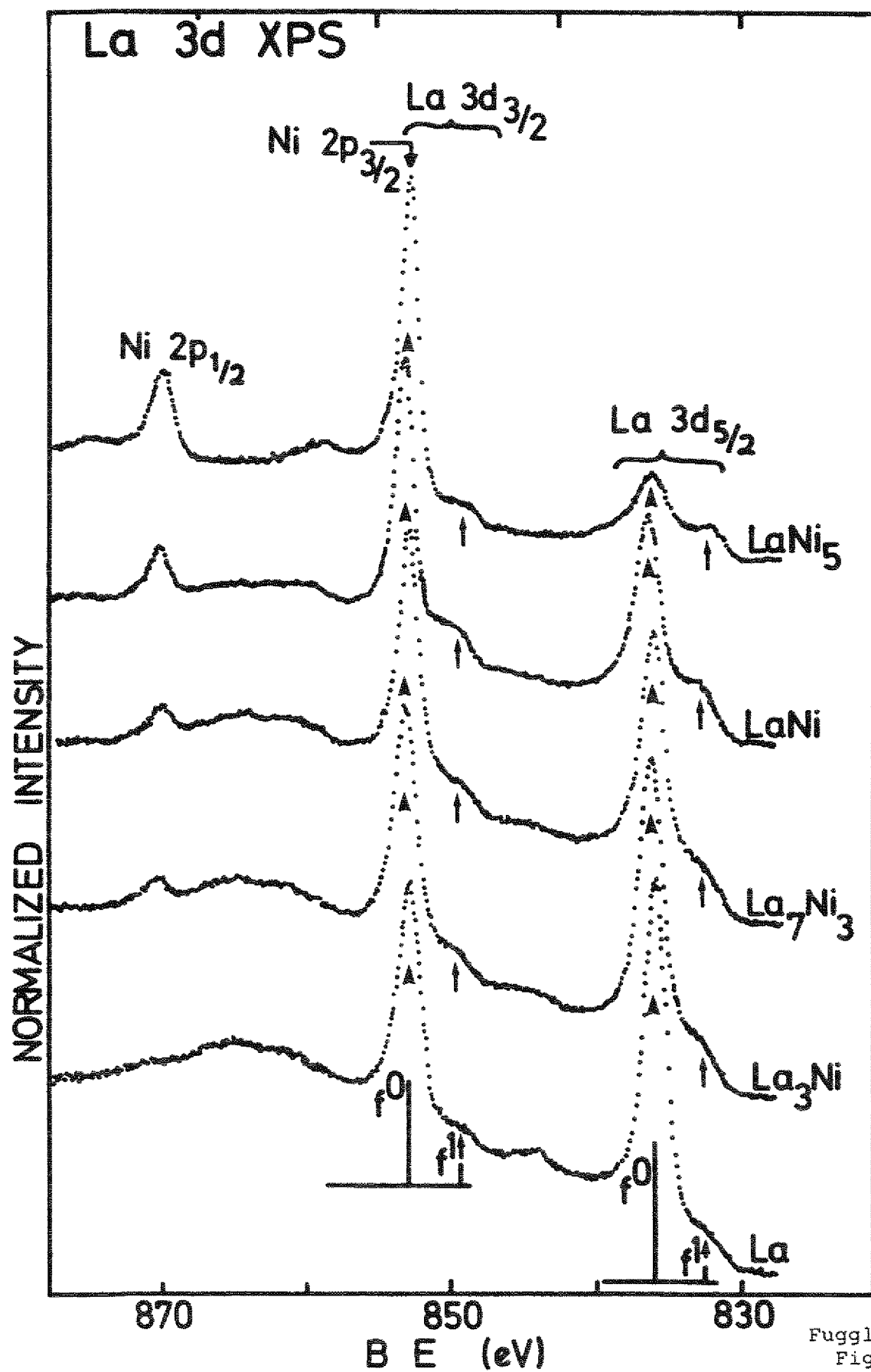
Fuggle et al
Fig. 5



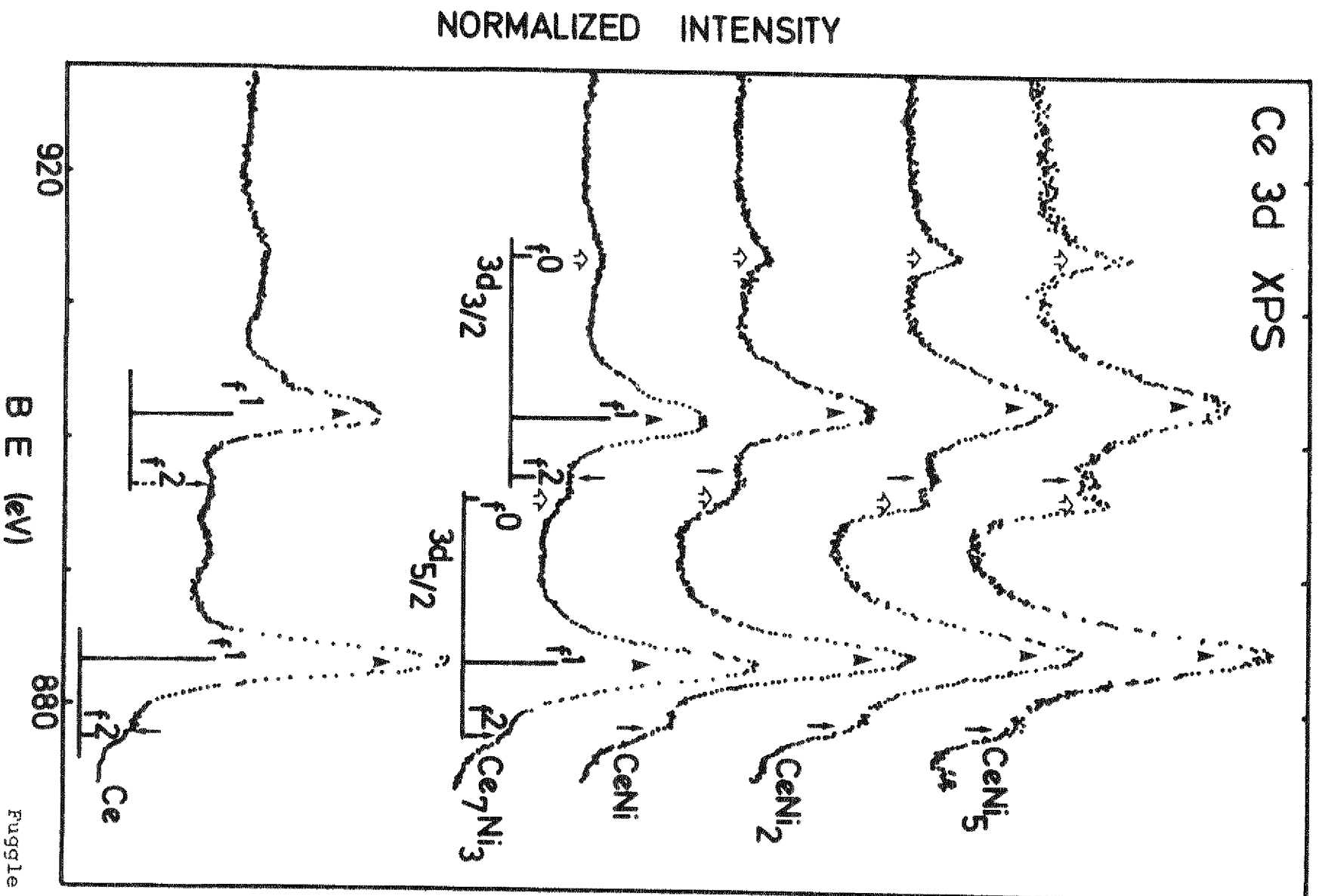
Ruggle et al
Fig. 6



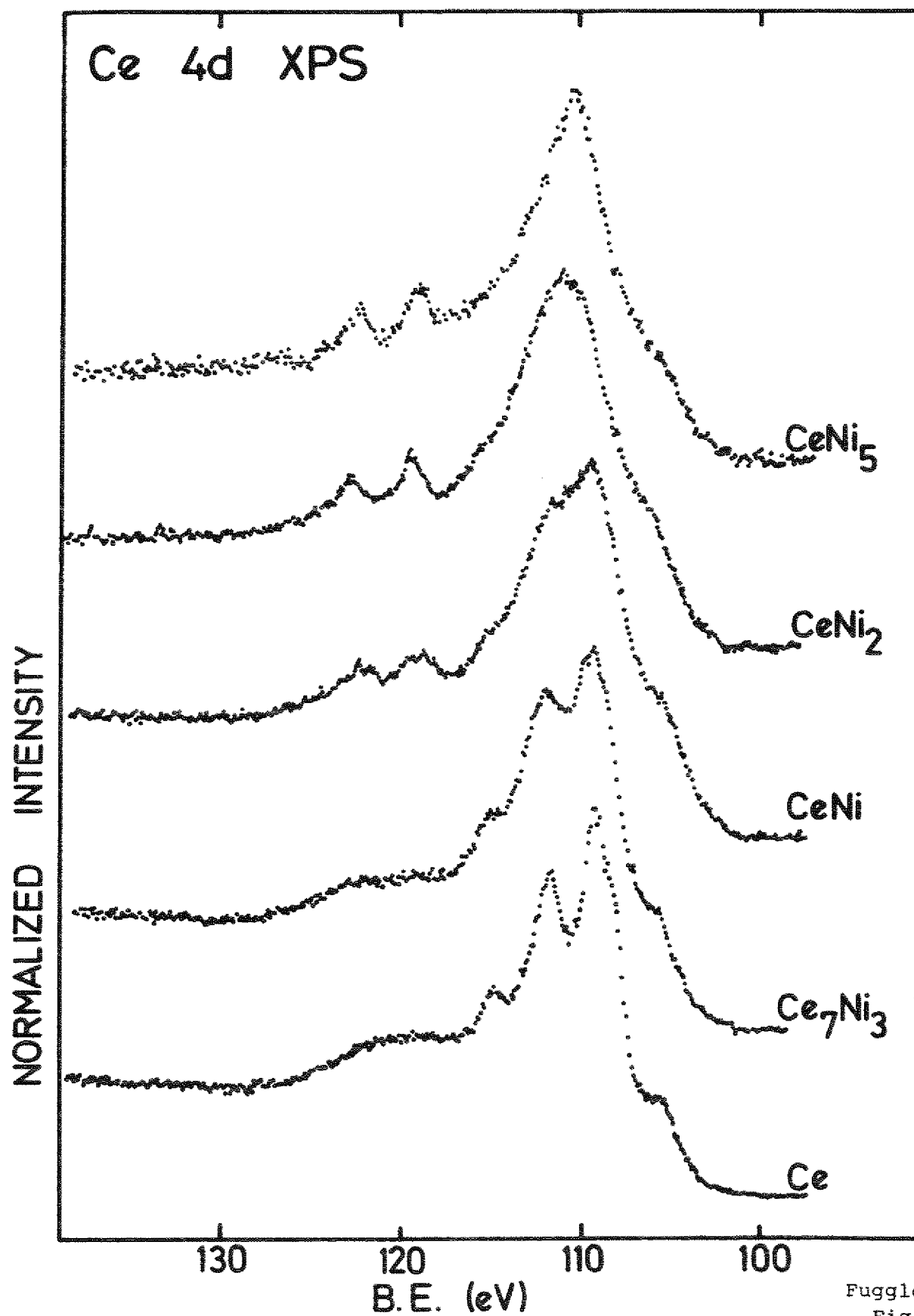
Fuggie et al
Fig. 7



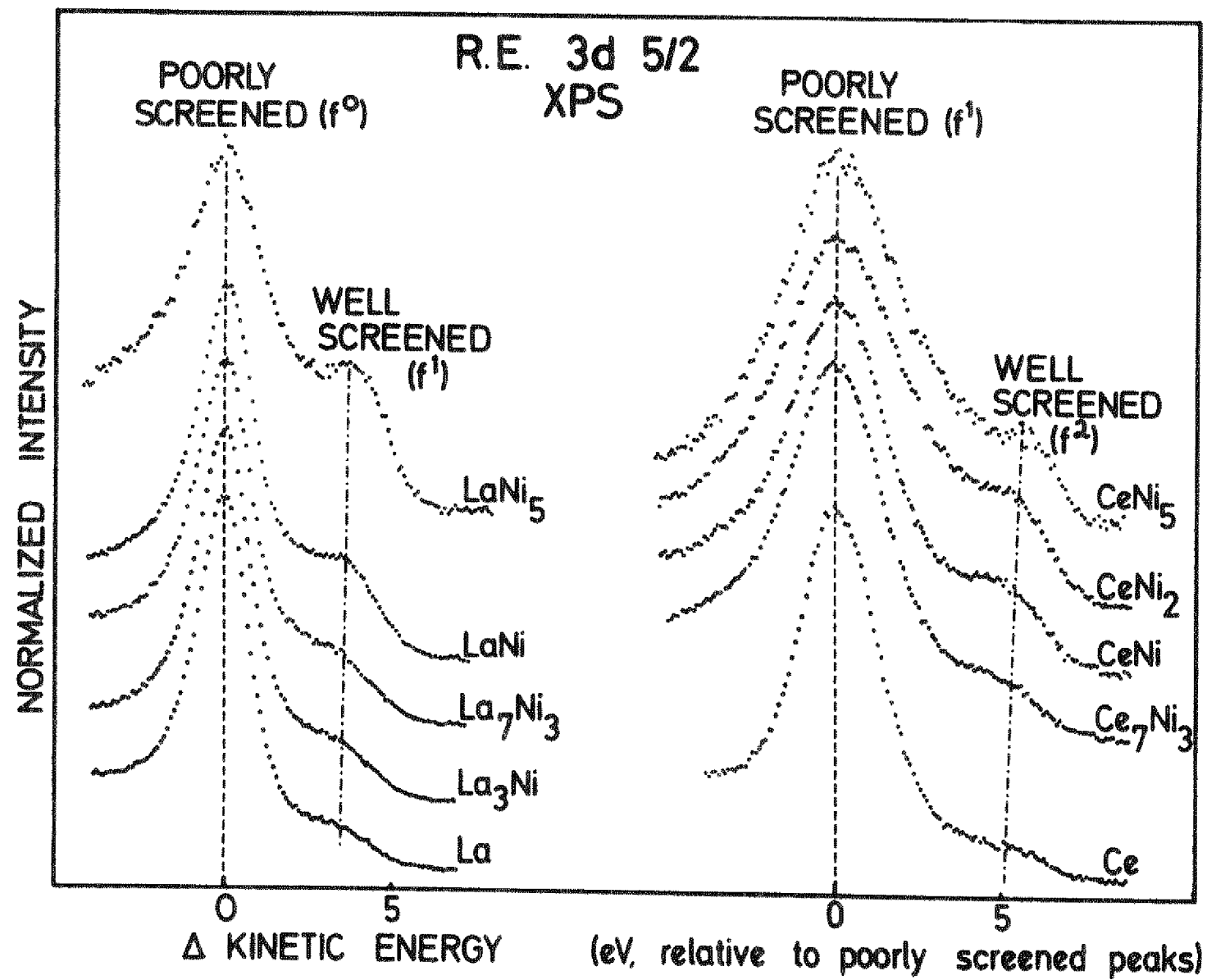
Fuggle et al
Fig. 8



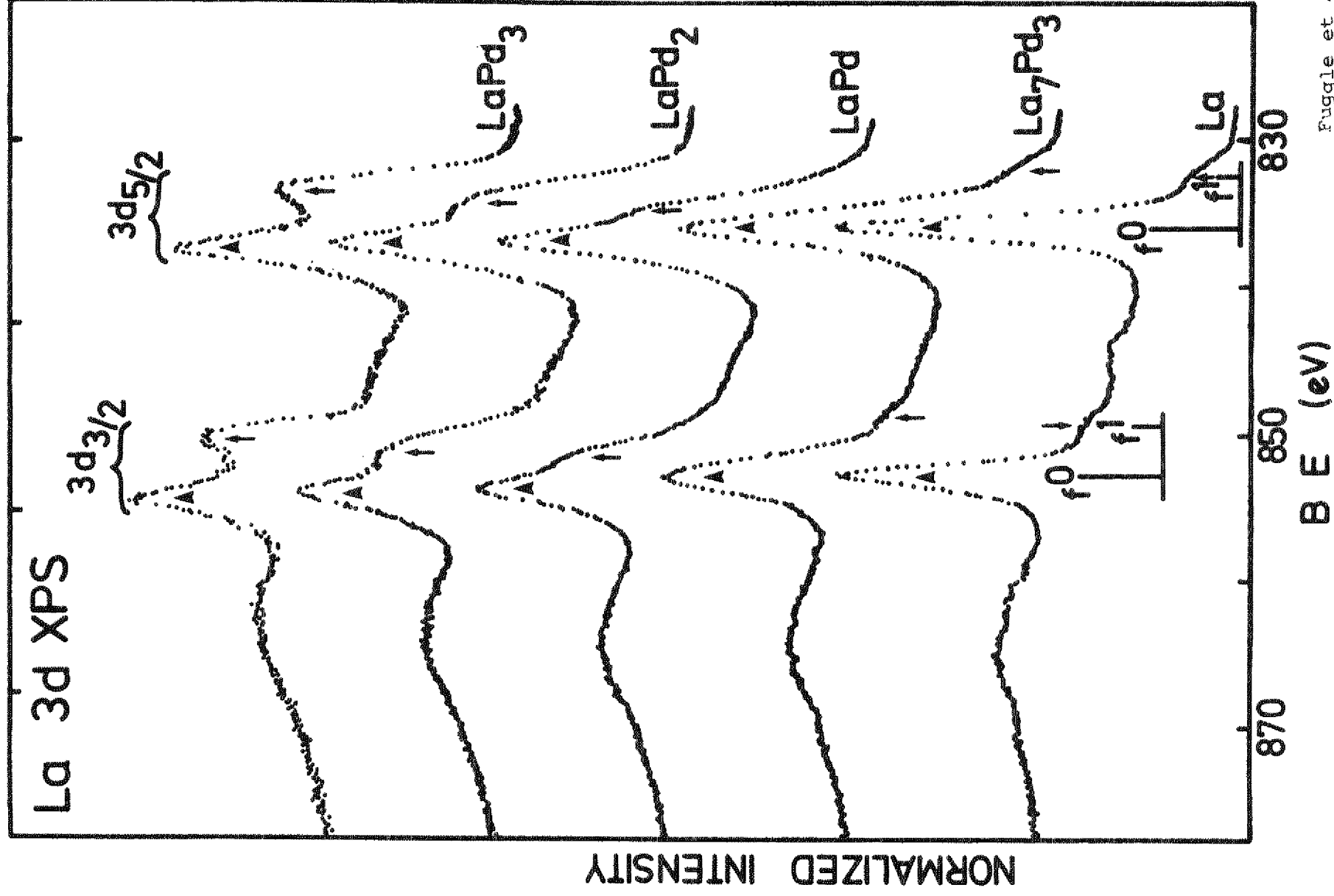
Fuggle et al
Fig. 9



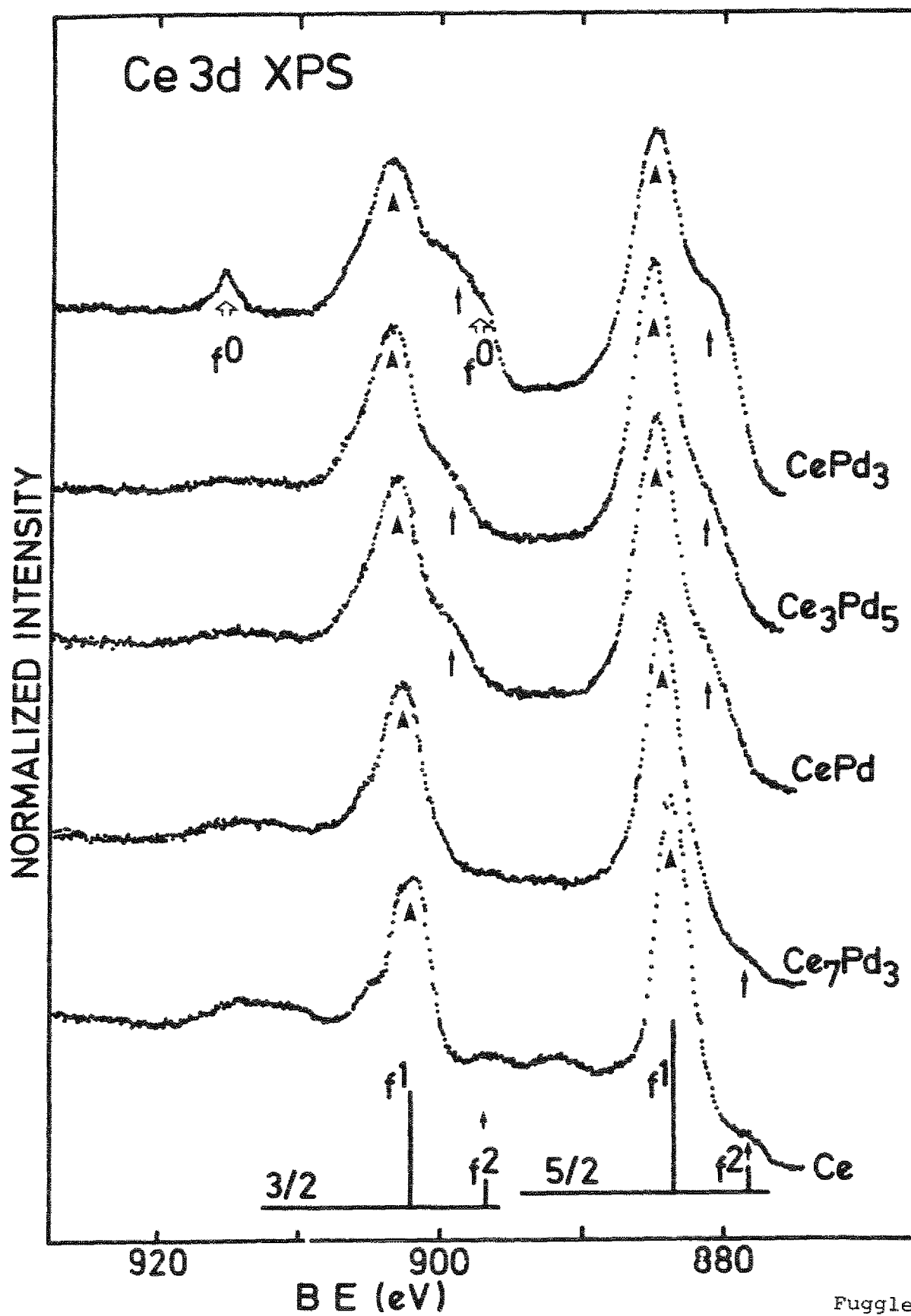
Fuggle et al
Fig. 10



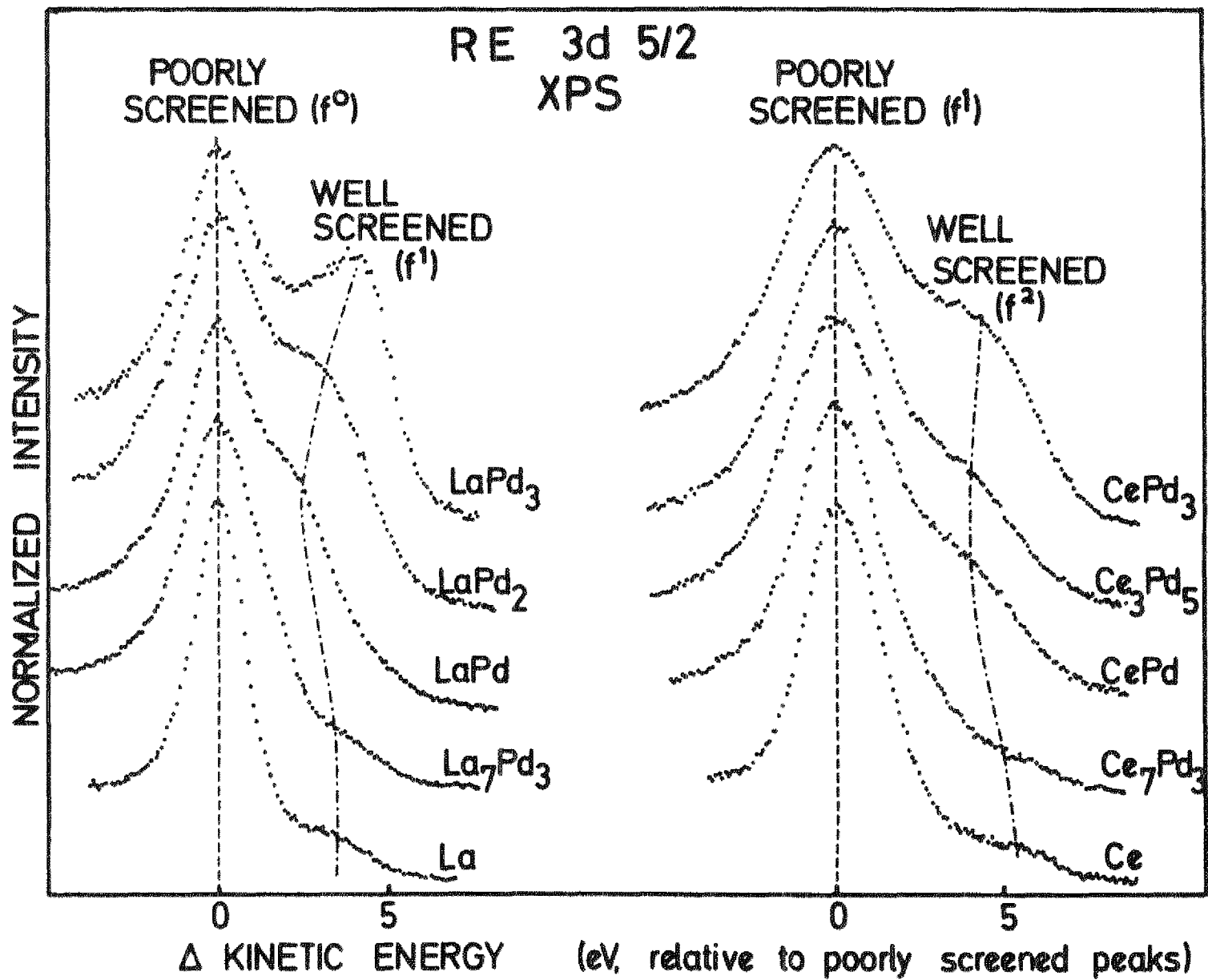
Fuggle et al
Fig. 11



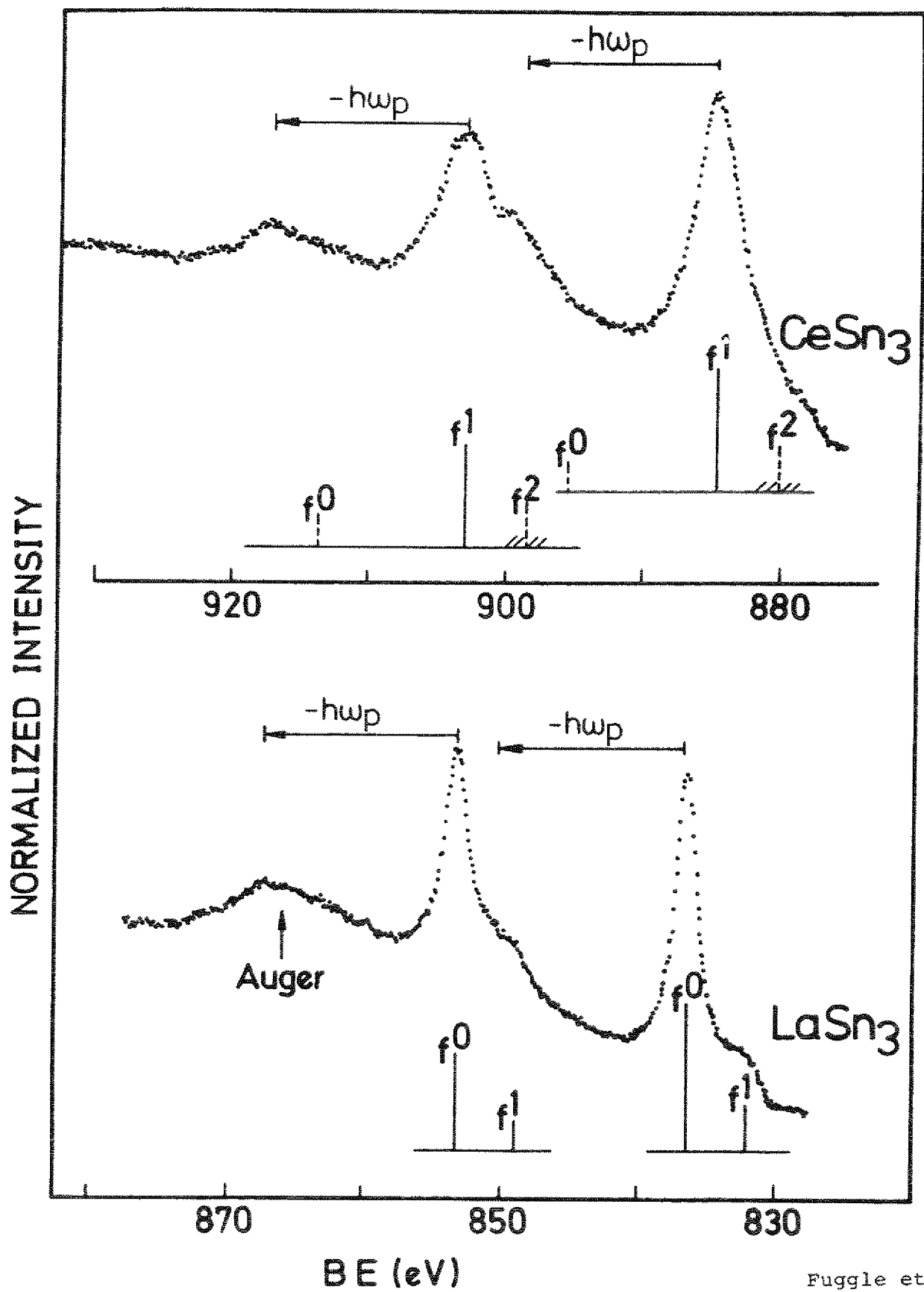
Fuggle et al
Fig. 12



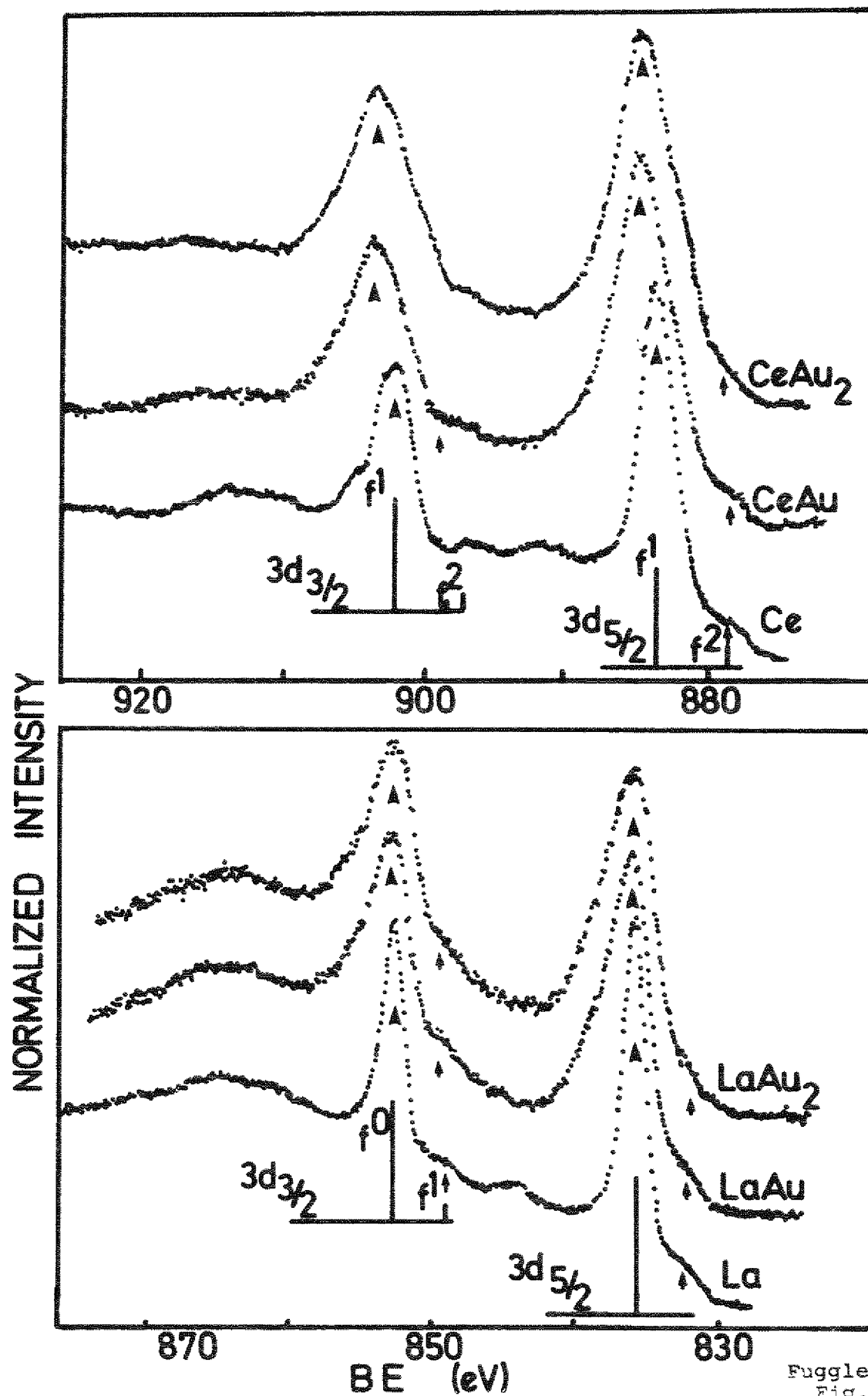
Fuggle et al
Fig. 13



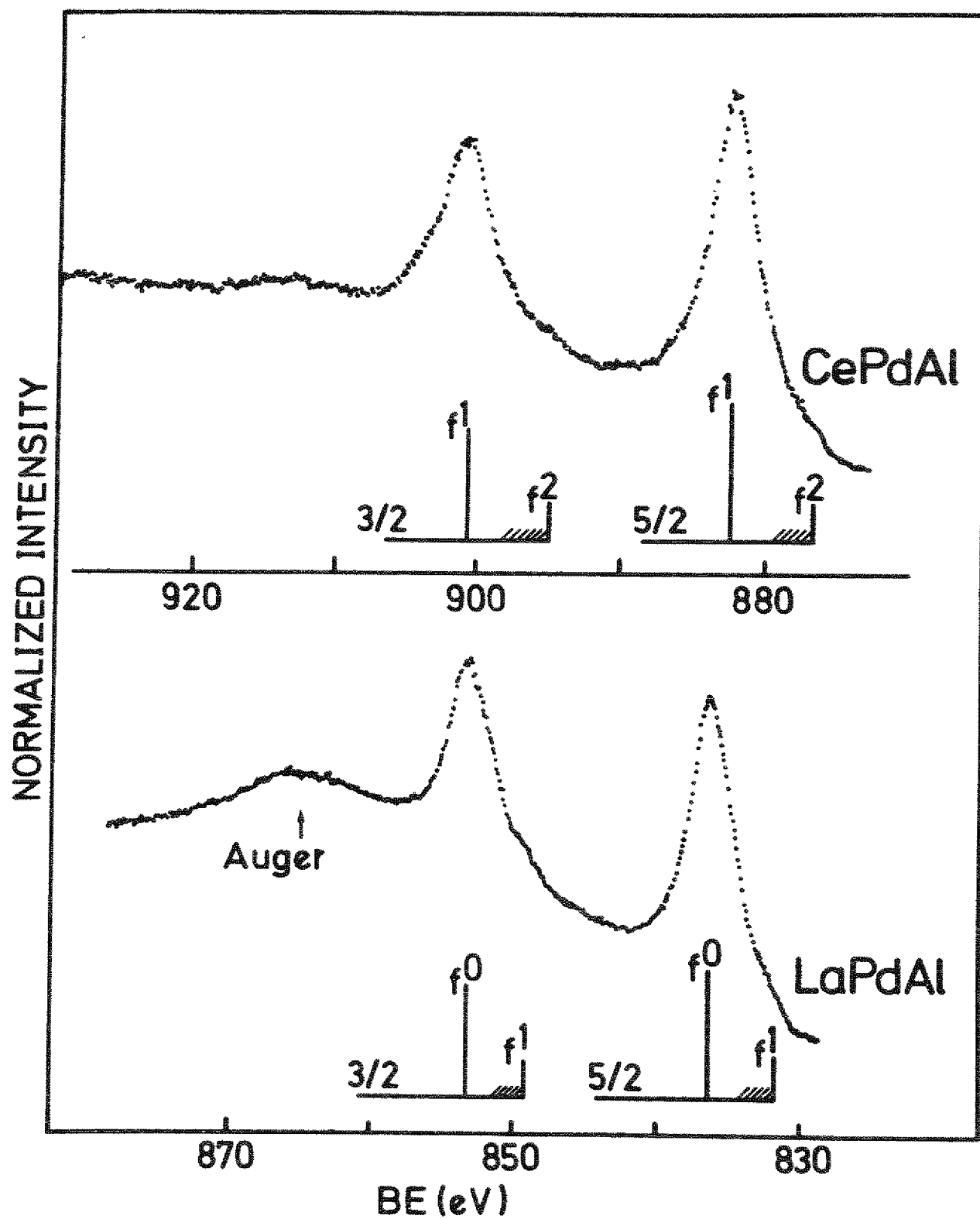
Fuggle et al
Fig. 14



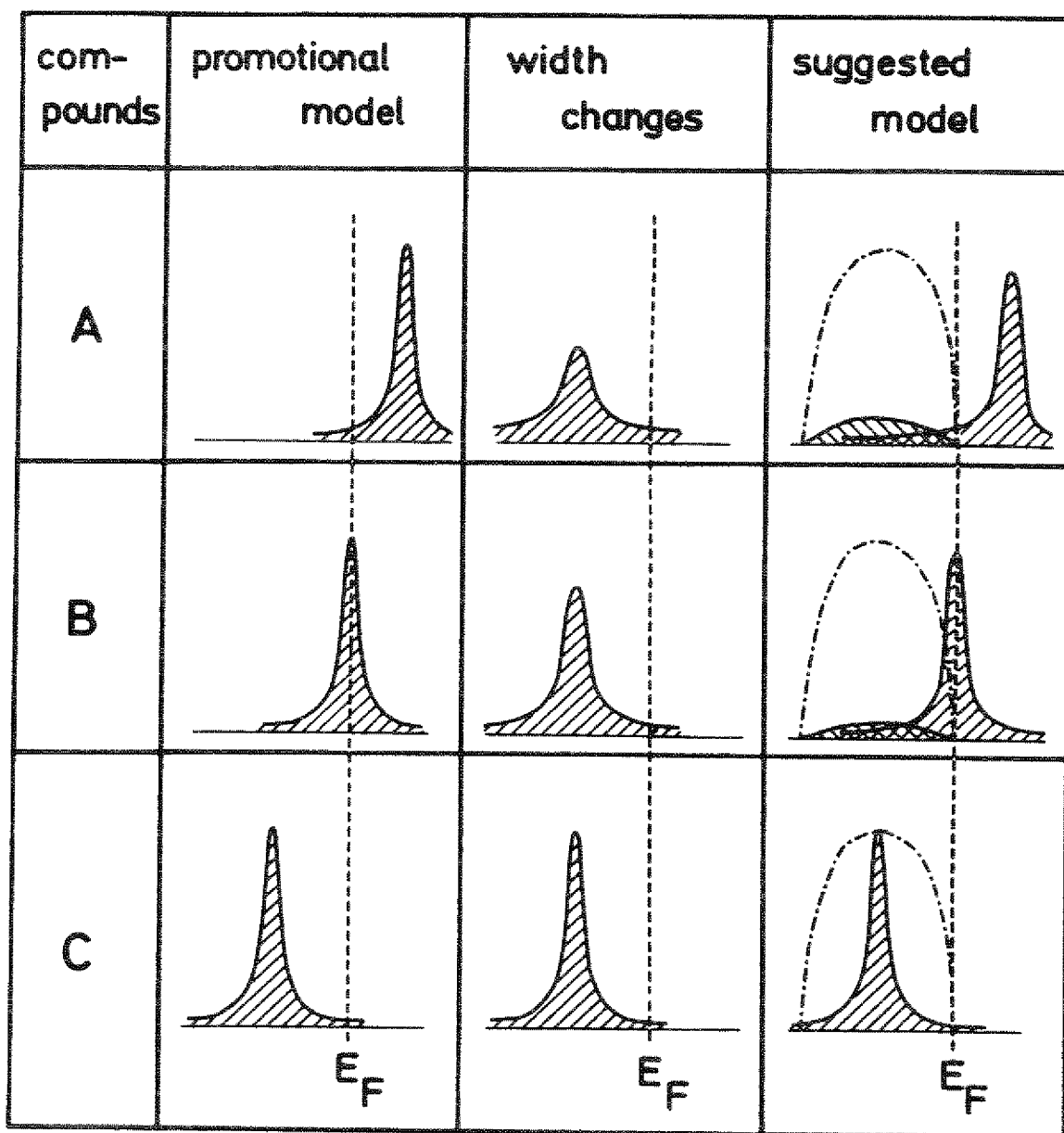
Fuggle et al
Fig. 15



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Fig. 16



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Fig. 17



Fuggle et al
Fig. 18



