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Transition to nonmagnetic f states in Ce intermetallic compounds studied by bremsstrahlung isochromat spectroscopy

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Bremsstrahlung isochromat spectra (BIS) of La and Ce intermetallic compounds with Co, Ni, Pd, Ru, Pt, and Au are presented. Final states with one and two f electrons are detected in trivalent La and Ce compounds, respectively. In contrast, in nonmagnetic Ce compounds, such as many of those with transition metals, transitions to final states with both one and two f electrons are observed. From the positions of the Ce BIS peaks it can be inferred that the effective Coulomb correlation energy of the Ce f electrons is not strongly dependent on chemical environment, and in all cases studied it is much larger than the hybridization width. The weights of the BIS f^1 and f^2 final states are not the same as those found in x-ray absorption (XAS) or x-ray photoemission (XPS) spectroscopies. From this it must be concluded that the f states are appreciably hybridized with the conduction states, and the necessity of a dynamic many-body description of the spectroscopic data (and consequently also of the Ce ground state) emerges clearly once more. We show that the discrepancy between XPS, XAS, and BIS intensity can be greatly reduced by calculations based on an extended Anderson model using the same set of parameters for all techniques and imply that this model must contain much of the relevant physics. The comparison of theory and experiment leads us to infer a hybridization Δ of the f levels which exceeds those accepted thus far by a factor of 5–10.

I. INTRODUCTION

Cerium and its compounds show many anomalous structural, magnetic, and other properties which do not fit into simple patterns and for which no quantitative explanations exist.[1–5] For instance the lattice constants of α-Ce and many Ce intermetallics are smaller than values extrapolated from the adjacent elements La or Pr. Anomalously large low-temperature specific heats and temperature-independent resistivities are often found. It is generally recognized that the Ce $4f$ electrons are in some way responsible for these anomalies. These electrons are quite strongly localized and well correlated. However, the Ce $4f$ electrons do not always have a localized magnetic moment or order magnetically at low temperature, which would be expected for strongly correlated electrons.[6] Various ideas have been put forward to try to explain the properties of Ce and its compounds including promotion of a $4f$ electron to the $5d6s$ states, partial promotion or mixed-valence,[1–5] Mott transitions to itinerant $4f$ electrons,[7] and Kondo-related effects.[8,9] The complexity of the observations suggests that probably more than one effect plays a role.

In such a situation it is desirable to have some experimental guidelines as to the relative sizes of the most important parameters, such as f-electron count, f-level binding energy, Coulomb correlation energy of the $4f$ electrons (U_{eff}), and the hybridization Δ between the f and the conduction states. Once this information is available, one is better able to choose which approximations and simplifications to incorporate in model calculations. To this end there have been many spectroscopic investigations of La and Ce compounds by x-ray photoemission spectroscopy[10–23] (XPS), x-ray absorption spectroscopy[18,19,24–27] (XAS), and resonant photoemission spectroscopy (PS) of the valence bands (VB).[28–32]

It has emerged from these studies that dynamical or many-body effects play a significant role in these spectroscopies.[22,23,27,33–38] Qualitatively, one finds in simple model systems that if hybridization (defined[33–35] as $\pi\rho_{\max}V^2$) is important in both the initial and final states, the intensity of the components closest to threshold in XPS, XAS, ultraviolet photoemission spectroscopy (UPS), or bremsstrahlung isochromat spectroscopy (BIS) is enhanced at the cost of the intensity in higher-lying components. The physical reason for this is that the wave function of the ground state contains a linear combination of the components with all coefficients of the same sign. The lowest-energy final eigenstate also has coefficients of the same sign, resulting in constructive interference for the intensity.

In connection with model calculations[34–36] a fairly consistent picture emerged of what can be learned from XPS, XAS, and UPS about the electronic structure of these materials.[23,27,36–38] The hybridization between the $4f$ and conduction states amounted to ~20–150 meV and, depending on the compound, was more important for the transition to nonmagnetic Ce than the decrease in f-electron count. In general the $4f$-electron count in Ce compounds was found to vary only between 0.8 and 1.05 in the compounds studied. However, this picture, relied heavily on core-level spectroscopy because $4f$ valence-band photoemission, is the most complicated of all to interpret.[30,35,36] For this reason we turned to BIS.

In BIS (Refs. 39–45) the sample is irradiated with monoenergetic electrons and the bremsstrahlung photons are detected at a fixed wavelength, while the energy of the incident electrons is scanned. At high energy (i.e., $h\nu \sim 1487$ eV was used here) the experiment can be considered as the time-reversed experiment to XPS, and it gives a spectrum related to the unoccupied density of states.[39–42] Of all the core- and valence-level spectroscopies, BIS has been the most neglected until now in both experimental and theoretical studies. It is already known that BIS spectra of Ce compounds depend strongly on the chemical environment of Ce and give quite direct information on the unoccupied states and the correlation energy U between f electrons.[43,44]

In BIS no core hole is created and a single electron is added to the system. One of the possible final states reached is one in which (to a first approximation) two electrons reside on the same site and we can speak of an f^2 final state. The second transition is often written $f^0 \rightarrow f^1$, stressing that the BIS peak intensity is most closely related to the weight $c(f^0)$ in the ground state. However, in this case the physical interpretation of the model we will use to explain BIS is that the local increase in f-electron density at any one site due to this BIS process in a solid is negligible. It is more correct to say that in Ce and its intermetallics an electron is added to a delocalized valence-band level near E_f, but that this transition is driven by an f-like matrix element whose intensity increases as the coefficient $c(f^0)$ increases.

The use of high-energy BIS to study the unoccupied $4f$ levels in Ce is especially appropriate because of the large degeneracy of the f states in this element.[42,43] While the f intensity in valence photoemission is proportional to n_f, the number of f electrons present in the ground state, the f contribution in the BIS spectrum is proportional to $N_f - n_f$, where $N_f = 14$ is the degeneracy of the f level. In this paper we concentrate on the Ce–transition-metal compounds with nonmagnetic Ce for which very low f-electron counts have been suggested in the past.[1–4] Here BIS has the additional advantage that the d bands of the transition-metal ligands are almost full so that the ligand contribution to the BIS spectrum is often small or negligible.

We present the BIS spectra from approximately 12 Ce intermetallic compounds and several La intermetallics used as control samples to help delineate which features in the spectra are due to the partner elements. In the discussion we first treat all conclusions that are possible without any model calculations and then go on to describe the results of model calculations which include many-body dynamical effects. We finally discuss what is learned from combining experimental and theoretical results.

II. EXPERIMENTAL

The BIS spectrometer is part of an XPS instrument equipped with a large solid-angle monochromator for Al $K\alpha$ radiation ($h\nu = 1486.7$ eV).[46] The electron gun is a cylindrical Pierce gun,[45,47] producing a wedge-shaped beam of up to 4.4 mA at 1500 eV. We used 300 A, and under this condition the beam has a rectangular cross section of 5×1.3 mm^2 at the sample[45] with an energy spread of 260 meV. The total resolution determined from the width of the signal rise from 10–90% at the Fermi level of Au is 650 meV.

The samples were prepared by melting the required quantities of the constituent metals in an induction-heated crucible under approximately 1 atm of pure Ar. They were characterized by metallography and x-ray diffraction. They consisted, in general, of 95–98% of the primary phase of the known crystal structures. The crystal structures are given in Refs. 5 and 48. Before the BIS experiment, the samples were cleaned by scraping in a vacuum of 1×10^{-10} Torr; during the BIS experiment with the cathode at the working temperature of 900 °C the pressure rose to 2×10^{-10} Torr. This is mainly due to electron desorption effects and even after extensive degassing and electron bombardment of the region around the electron gun it was not possible to work at lower pressures. Clearly the chief problem in all BIS measurements is to keep contamination effects to a minimum. Data were taken for no more than 30 min after scraping the samples. Because of the high collection angle of the monochromator the intensity was sufficient in all cases to identify the main spectral features and check for contamination. In all cases the sample was rescraped and the spectra remeasured and summed to improve the signal-to-noise ratio. The contamination of the sample surface was controlled by monitoring the O 1s and C 1s levels with XPS, and it was in general less than $\frac{1}{4}$ monolayer before and after the measurements. We did parallel studies of contamination effects to check that none of our observations were unduly distorted by contamination. The problem of graphite formation encountered by Lang *et al.*[41] was not found here.

III. RESULTS

A. La compounds

In Fig. 1 we present the BIS of a series of La-Ni compounds. The spectrum for pure La is the same as that of Lang *et al.*[43] The smooth intensity between the Fermi level and 12 eV is due to the $5d\,6s$ valence band, which is very wide,[49,50] and at higher energies inelastic losses also contribute.

When we add Ni to La the spectrum hardly changes. The f peak is shifted by small amounts to a higher energy; only in LaNi$_5$ is a 1.2 eV shift found. The numbers given in Table I show that the width w is constant for La and all compounds at 1.5 eV, with the exception of LaNi$_5$ where a slightly larger width is found. This may be due to the higher energy of the peak, a different density of states, or an increase of the hybridization. It should be noted that the lifetime broadening of a state above E_F in-

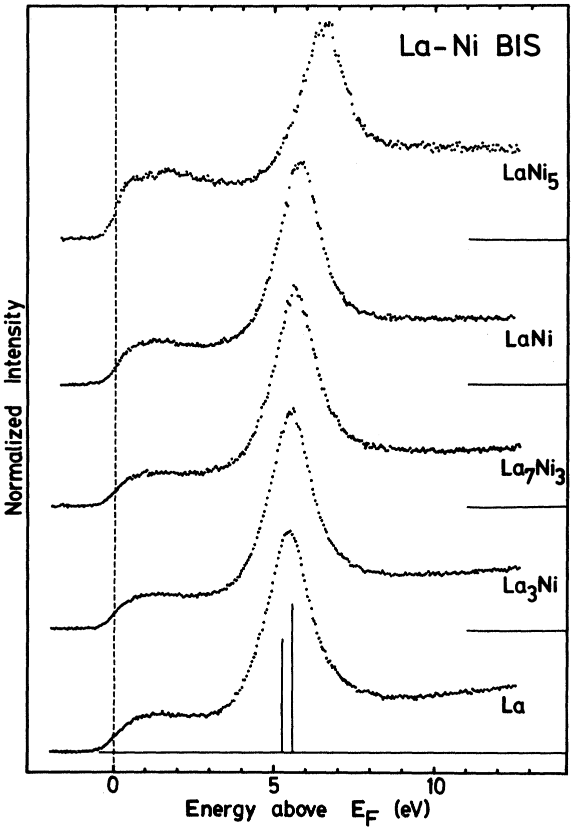

FIG. 1. BIS of La-Ni compounds. In LaNi$_5$ the structure at 1.8 eV is ascribed to empty La d and Ni d states. The La multiplet structure is taken from Ref. 43.

creases with its separation from E_F. For instance, in BIS measurements of the noble metals[51] it is found that the lifetime broadening increases by about 0.1 eV per eV above E_F and similar effects are discussed in Ref. 42. A 1.2 eV shift to higher energy, as in the $4f^1$ level of LaNi$_5$, may explain the increased width.

In the whole series of alloys we hardly find any evidence of the Ni content, although in LaNi and LaNi$_5$ the "background" seems to be uniformly higher than in pure La. This is probably due to the contribution of the Ni states. In LaNi$_5$ there is a broad bump at 1.8 eV, and the intensity increase from below to above the f^1 peak is higher than in all the other compounds. The bump at 1.8 eV in LaNi$_5$ is attributed to a split-off d state[52] made up mainly of La d character.[53] Because of the low La content its intensity is small, and it is not necessary to account for the corresponding peak in CeNi$_5$ when determining the $f^1 : f^2$ intensity ratio. The increased intensity above 8 eV is probably due to Ni 4s and 4p states[53] which also lead to a rise in the BIS spectrum of pure Ni and noble metals at $\sim$5.5 eV.

An important result is that the empty part of the Ni d band, which in Ni leads to an intense narrow line just above E_F (Refs. 40 and 54), is not observed in La-Ni compounds, even at the highest Ni concentration of 83%. The low-temperature specific heat of R-Ni$_5$ (R denotes rare earth) compounds is only reduced by 20% compared to Ni (Ref. 55), so there must be some states at E_F. However, the total number of unoccupied d states is drastically reduced compared to Ni (Ref. 48), so that their weight is too small to show up in BIS with an instrumental resolution of 0.65 eV. Band-structure calculations for YNi$_5$ and LaNi$_5$ (Ref. 53) indicate that the Ni d band in these compounds has fewer holes than in Ni, but show that there is still a density of d states at the Fermi level comparable to Ni, in agreement with the specific-heat results.

B. Ce compounds

In Fig. 2 the BIS of a series of Ce-Ni compounds are shown. Peak energies and relative intensities are given in Tables I and II. The Ce spectrum is the same as that of

TABLE I. Positions and full widths at half maximum (w) of f^1 and f^2 peaks in La and Ce intermetallic compounds (all values in eV).

	La analog		Ce analog				
Material	ϵ_{f^1}	w	ϵ_{f^1}	w^1	ϵ_{f^2} peak	ϵ_{f^2} shoulder	w
R	5.45	1.5	0.6		4.0	5.5	3.3
R^a	5.5	1.4			4.0	5.6	3.3
R_3Ni	5.5	1.5					
R_7Ni$_3$	5.6	1.5	0.6	0.7	4.4	5.9	3.3
RNi	5.75	1.5	0.6	1.05	4.65	6.2	3.3
RNi$_2$			0.65	0.9	5.0	6.6	3.4
RNi$_5$	6.55	1.6	0.6	0.9	5.75		(2.7)
CeCo$_2$			0.65	1.0	5.65		3.4
CeCo$_5$			0.75	1.0	5.7		2.9
RRu$_2$	6.2	1.7	0.9	1.15	5.85		3.5
Ce$_7$Pd$_3$					4.2	5.85	3.1
Ce$_3$Pd$_5$					4.45	5.95	2.6
RPd$_3$	6.3	1.6	0.6	0.7	5.05	6.70	2.8
CePt$_3$			0.6	0.8	5.1	6.4	2.7
CeAu					4.1	5.6	2.9

[a] Reference 43.

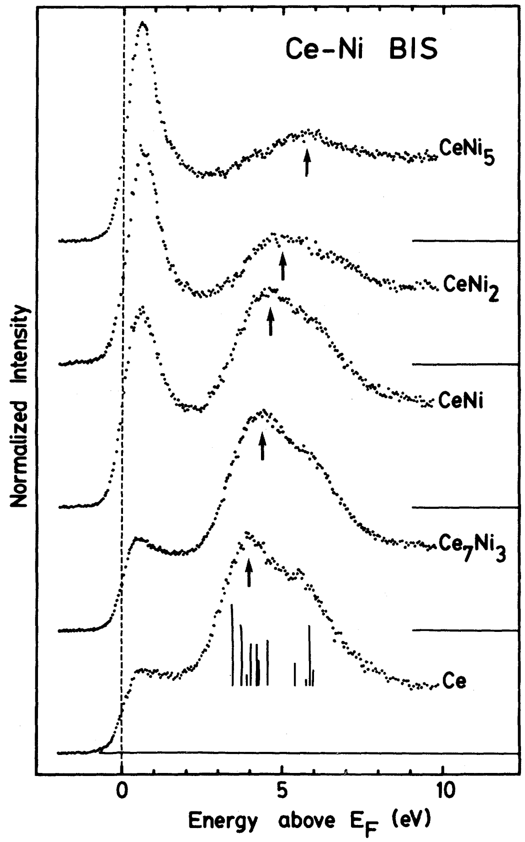

FIG. 2. BIS of Ce-Ni compounds. The Ce multiplet structure is taken from Ref. 43.

Lang *et al.*[43] The lowest unoccupied states are (5*d*6*s*) valence states forming a wide band.[49,50] This leads to a more or less uniform signal up to 8–10 eV. Between 2.5 and 7 eV there are transitions to an f^2-like final state. The peak is at 4.0 eV, and there is a shoulder at 5.4 eV. The shape reflects the multiplet structure of the f^2 final state.

In the alloys with Ni the f^2 final state is shifted to higher energies and its intensity is reduced. Although the BIS of $CeNi_5$, for instance, shows a relatively weak f^2 peak its integrated intensity is about the same as that of the f^1 peak. (See the Appendix for comments on evaluation of peak areas.) As the f^2 peak decreases a peak starts to develop immediately above E_F and gains weight with increasing Ni content. A small peak is found even in pure γ-Ce.[44] From XPS and XAS we know that there is an f^0 contribution to the ground state CeNi, $CeNi_2$, and $CeNi_5$. The ground state is a mixture of f^0 and f^1 and a small amount of f^2. Adding an electron can lead to "f^1"- and "f^2"-like states.[56] The f^1 final state, being a major component of the ground state, must be located near E_F. The peak at E_F cannot be due to empty Ni *d* states, because we have seen from the La-Ni BIS that the empty Ni *d* states do not give rise to large BIS intensity. We thus interpret the peak at E_F as being due to transitions to an f^1 final state.

We note that the shoulder at about 1.5 eV higher than the peak of the f^2 is still clearly visible in CeNi, and a weak indication of it is probably present in $CeNi_2$. Looking at the whole series, we note that the details of the multiplet structure become increasingly smeared out with increasing Ni content. For $CeNi_5$ the f^2 peak is rather structureless. However, it is difficult to decide whether the disappearance of the structure in the f^2 peak is only due to a decrease of intensity, or whether the broadening becomes very large. The measured width given in Table I is also not a good guide because it is very difficult to measure, especially if there are broad but weak tails.

Figure 3 shows the BIS of some Ce-Pd compounds. The f^2 is shifted upwards when Pd is added. In contrast to Ni compounds, no peak at E_F is seen except at a high

TABLE II. Experimental ratios $I(f^1)/I(\text{tot})$ from BIS compared with experimental results of 3*d* XPS and 3*d* XAS. The two values given for BIS result from different background subtractions as detailed in the Appendix, and illustrate the uncertainty range for the experiment.

Material	$I(f^1)/I(\text{tot})$ (BIS)	$I(f^0)/I(\text{tot})$ (3*d* XPS, Ref. 23)	$I(f^1)/I(\text{tot})$ (3*d* XAS, Ref. 27)
Ce	0.02–0.07	<0.04	~0.02
Ce_7Ni_3	0.03–0.13	<0.04	
CeNi	0.21–0.22	0.02	
$CeNi_2$	0.44–0.42	0.06	0.11
$CeNi_5$	0.62–0.54	0.12	0.08
$CeCo_2$	0.66–0.52	0.10	
$CeCo_5$	0.61–0.56	0.07	
$CeRu_2$	0.64–0.52	0.12	
Ce_7Pd_3	~0.0	<0.04	
CePd		<0.04	<0.02
Ce_3Pd_5	~0.0	<0.04	<0.02
$CePd_3$	0.17–0.16	0.05	0.06
$CePt_3$	0.21–0.23	0.10	
CeAu	~0.0	<0.04	<0.02
$CeAl_3$[a]	~0.0		
$CeSn_3$[a]	~0.0	<0.06	<0.02

[a] Reference 44.

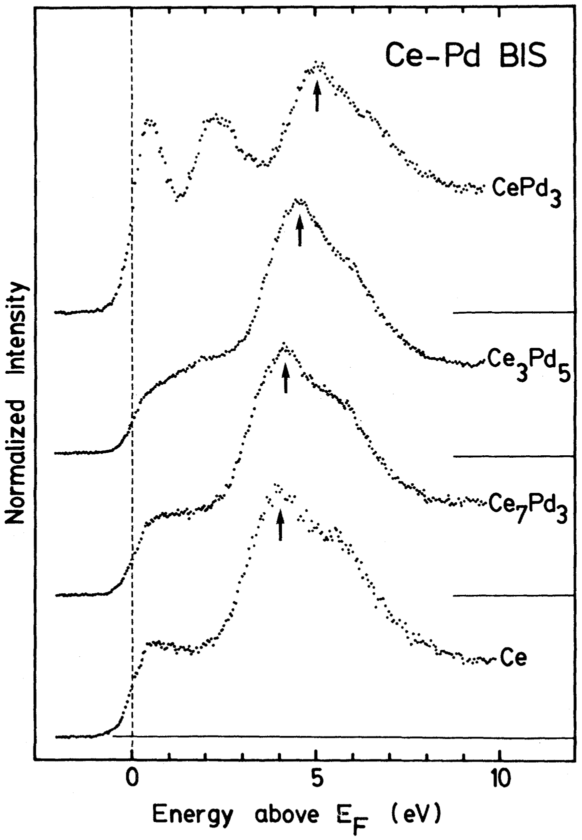

FIG. 3. BIS of Ce-Pd compounds. The peak at 2.3 eV in $CePd_3$ is due to *d* states.[52]

concentration of Pd in $CePd_3$. In $CePd_3$ there is also a peak at 2.3 eV above E_F. As we have shown earlier,[52] it is due to Ce and Pd *d* states and can be neglected if we are interested in the *f* level. The BIS result is in qualitative agreement with the XPS results for these compounds, because $CePd_3$ was the only Ce-Pd compound where an f^0 contribution to the ground state was found.[16,19,23,27]

In Ce_7Pd_3 and Ce_3Pd_5 the intensity in the region between E_F and the f^2 signal is increased compared to Ce. This feature shows the development of a narrow band of mainly Ce 5*d* character, which becomes clearly visible as a split-off band in $CePd_3$.[52]

In Fig. 4 BIS spectra of some miscellaneous, but nevertheless very interesting, Ce compounds are shown. CeAu does not show any evidence of f^1; the f^2 moves to a slightly higher energy than in Ce, and the total width of the f^2 is reduced, perhaps because of the low density of Au states in this region. The Au does not seem to affect the overall appearance of the spectrum very much. However, there is a slight decrease in intensity near E_F which was also found earlier in $CeAl_3$.[44] This may indicate that there is a small f^1 contribution to the spectrum of γ-Ce which is decreased in some alloys. In $CePt_3$ (Ref. 57) an intense f^1 peak is found, and the f^2 moves up by 1.1 eV. As the Pt *d* bands are seen to be full in the XPS spectrum of $CePt_3$ we conclude that these do not contribute to the BIS, but there may be a contribution of the Ce 5*d* bands as seen in $CePd_3$.

The materials $CeRu_2$, $CeCo_2$, and $CeCo_5$ are also very interesting and the first two become superconducting at 6.2 and 1 K, respectively.[58,59] On that basis one might conclude that there is no *f* electron in these compounds, i.e., that the *f*-electron count is zero. This conclusion was based on the assumption that an *f* electron should have a magnetic moment which would destroy the superconductivity. The BIS show that the f^2 peaks are weak, while the peaks at E_F are very intense, pointing to a large f^0 contribution to the ground state. Ru has ~3 holes and Co ~2.4 holes in the *d* band,[60,61] and it is impossible to fill these holes with Ce electrons. There is a large density of transition-metal *d* states at E_F, as seen in the XPS spectra. The BIS peak at E_F therefore contains some unoccupied *d* states of the transition metal, which also leads to the higher f^1 peak intensity. A correction for these *d* states brings us even further away from the presumed f^0 ground state.

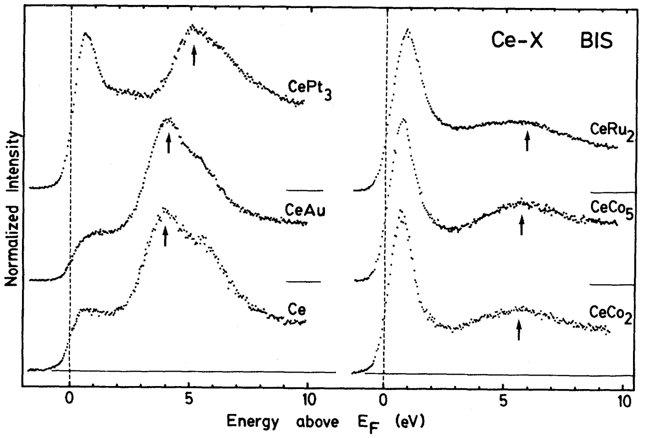

FIG. 4. BIS of magnetic γ-Ce and CeAu and nonmagnetic $CePt_3$, $CeRu_2$, $CeCo_5$, and $CeCo_2$.

IV. DISCUSSION

A. Interpretation

As most of the discussions of the properties of Ce and its compounds have centered around the *f*-electron count then let us assume for the moment that the ground state is a mixture of f^0 and f^1 states. As discussed in the Introduction on BIS, the addition of an *f* electron should lead us to f^1 and f^2 final states, just as in XAS at the 3*d* edges[27] while in core-level XPS we would expect f^0 and f^1 final states. The first point to be settled is whether our BIS peak assignment is correct. We expect the f^1 and f^2 final states to be separated by approximately the Coulomb correlation energy *U* for the two *f* electrons, which is estimated to be 5 eV.[62,63] Since $\Phi(f^1)$ is a major component of the ground state we expect the f^1 peak near E_F and the f^2 peak to be about 5 eV higher.[64] We note that in all those cases where we find a $3d^9 4f^0$ final state in XPS, we also find a peak at E_F in BIS. The BIS of Ce_7Ni_3 clearly shows a peak at E_F, although in XPS the $3d^9 4f^0$ final state could not be recognized. However, a small f^0 in XPS may be there, and an enhancement of the f^1 final states in BIS can lead to a structure with the experimentally observed intensity. $CePd_3$ shows three peaks, but it has been demonstrated that the peak at 2.3 eV is due to Ce 5*d* (and Pd 4*d*) states, and the remaining two peaks at E_F and at 5.05 eV can be interpreted as transitions to f^1 and f^2 final states.[44,52] By comparing the Ce-Ni and $CePd_3$ spectra with the La analogs, we realize that there are no empty transition-metal *d* states in most Ce-Ni and Ce-Pd compounds. We thus conclude that our assignment is justified.

The next point to be considered is the size of U_{eff} (Ref. 63) and whether the transition from magnetic to nonmagnetic behavior in Ce compounds can be correlated with changes in U_{eff}. As formulated by Hubbard,

$$U_{\text{eff}} = V_{\text{ion}} + A_e \ , \tag{1}$$

where V_{ion} is the ionization potential of the 4*f* level (ϵ_f) and A_e is its electron affinity. We do not know ϵ_f exactly but it can safely be assumed to be between 0 and 2 eV.[28–32,62,65] The electron affinity of the *f* level is defined to a first approximation by the f^2 peak position. This is between 4.0 and 5.85 eV in the compounds measured. Thus there is some room for variation of U_{eff} allowed by our results, but it is clear that it does not "collapse" to less than the 4*f* hybridization width in any of the compounds studied. Thus variations in U_{eff} alone cannot explain the transition from magnetic to nonmagnetic behavior in Ce compounds.

Finally we consider the meaning of the relative f^1 and f^2 BIS peak intensities. There are certainly difficulties in subtracting a sensible background. We have adopted two different procedures, as detailed in the Appendix, to obtain an idea of the uncertainties involved. Both sets of intensity ratios are given in Table II. They do agree reasonably well, although in some cases a difference of $\sim 10\%$ is found and this is significant. The ratio of the f^1 to total *f* BIS peak intensity does not reach one, as would be expected if so-called tetravalent Ce atoms were present in the samples. Also listed in Table II are the corresponding ratios of $I(f^0)/I(\text{tot})$ for XPS and $I(f^1)/I(\text{tot})$ for 3*d* XAS from Refs. 23 and 27. There are large differences between the BIS, XAS, and XPS values which cannot be explained by experimental uncertainties. It is well known from simple model calculations that ground-state populations can only be determined directly from XPS, XAS, UPS, and BIS if the energy separation of the components in the final state is very much larger than the hybridization parameters.[22,23,27,34–38] We can therefore conclude that hybridization is important for the Ce 4*f* levels. Qualitatively one finds in simple model systems that if hybridization is important in both the initial and final states, the intensity of the components close to threshold in any of the above spectroscopies is enhanced at the cost of the intensity of higher-lying components.[66–75] This is exactly what is observed in the data of Table II.

To interpret the intensity data more fully the computation of the BIS of Ce compounds within an Anderson impurity model, which has been described elsewhere,[34,35] was used. Here we give an account of the results of such calculations as they are relevant to the experimental observations. The parameters entering in the calculation are the Coulomb interaction between the *f* electrons, *U*, the position of the bare *f* level, ϵ_f, and the hybridization between the *f* levels and the conduction states, $\Delta = \pi\rho_{\max}V^2$. In this definition *V* is the hybridization matrix element and $\rho_{\max}$ is the maximum density of conduction states. The calculation of the spectra leads to final states with approximately one and two *f* electrons. Within our model the shape of the BIS was found not strongly dependent on the particular form of the density of states chosen.

The *f*-electron count and the weights of the f^0, f^1, and f^2 wave functions in the ground state depend on both ϵ_f and Δ. The intensity and positions of the f^1 and f^2 BIS peaks also depend on *U*. If we neglect interaction between the f^0, f^1, and f^2 states, the f^2 peak is located at $E = 2\epsilon_f + U - \Delta E$ and the f^1 peak is located at $\epsilon_f - \Delta E$, although BIS only gives f^1 intensity above E_F. ΔE is the difference between the ground-state energy and the energy of the lowest state with the *f* level empty. $\Delta E - \epsilon_f$ is then the contribution of hybridization and is rather small for the systems considered. Without coupling the f^1 and f^2 BIS peaks would have the weights $N_f c(f^0)$ and $(N_f - 1)c(f^1)$, respectively, where N_f is the degeneracy of the empty *f* level and the $c(f^n)$ are the squares of the coefficients of f^n in the ground-state wave function. The hybridization leads to coupling between the peaks with a *large transfer of weight from the* f^2 *peak to the* f^1 *peak* and an increase in the separation of the two peaks. This is shown graphically in Fig. 5 where the BIS intensity ratio $[I(f^1)/I(\text{tot})]$ is plotted as a function of $c(f^0)$ for three values of Δ. Also shown are the corresponding curves for XPS $[I(f^0)/I(\text{tot})]$ and XAS $[I(f^1)/I(\text{tot})]$ for $\Delta = 120$ meV. Note that deviations from linearity are in the opposite direction in BIS and in XPS or 3*d* XAS.

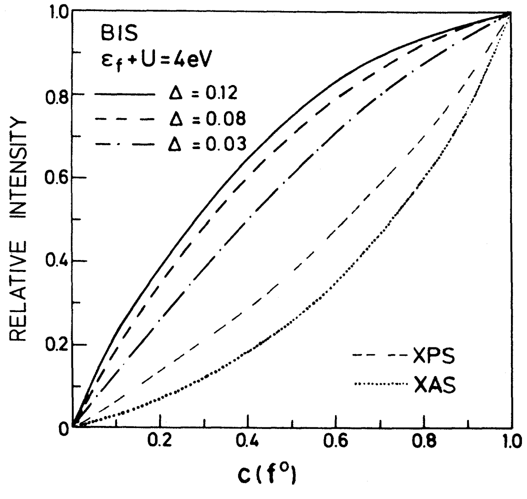

FIG. 5. Relative intensity of the f^1 peak for BIS as a function of $c(f^0)$ for three values of Δ. Also given are the corresponding curves for f^0 peak intensity in XPS and f^1 peak intensity in XAS with $\Delta = 120$ meV. We have used a semielliptical *d* band $F(\epsilon) = 2V^2[B^2 - (\epsilon - \epsilon_0)^2]^{1/2}/B^2$, where $B = 2.785$ eV, $\epsilon_0 = -1.215$ eV, and $\Delta = 2V^2/B = 120$ meV. The value of ϵ_f was varied between -2.6 eV $[c(f^0) = 0.05]$ and -0.2 eV $[c(f^0) = 0.52]$. Details of construction of these curves are given in Ref. 23.

B. Combination of experimental and model results

Here we discuss some of the important technical points needed for detailed analysis of the spectra and assessment of their relationship to magnetic effects in Ce compounds. The first question to be addressed is whether the model used can explain the discrepancies in intensity ratios in BIS, XPS, and $3d$ XAS. To help judge this point we give in Table III the values of $c(f^0)$ derived from the peak ratios for the various techniques as shown in Table II and Fig. 5. These values are derived using the hybridization Δ obtained from XPS spectra. There is usually an ambiguity of $\pm 20\%$ in determination of Δ from the spectrum but there may be systematic errors on top of this which can lead to additional uncertainty in $c(f^0)$ of $\pm 20\%$. Nevertheless, it is perfectly clear that many of the discrepancies in peak ratios listed in Table II disappear when we include the dynamics of the spectral process by using Fig. 5. Even for the worst cases the discrepancies are substantially reduced and hardly exceed the experimental error. The remaining discrepancies give an indication of the quality of the simplifying assumptions necessary to make the theory tractable. The most important simplifications are as follows.

(1) The hybridization was assumed to be independent of the f occupation and the presence of a core hole.

(2) The dilute impurity limit was assumed.

(3) Auger decay of the f^1 and f^2 configurations was neglected.

(4) Transitions of the incoming electrons to the $5d$ states were neglected.

(5) It was assumed that an f hole is always screened. An f-d interaction can therefore be implicitly included as a reduction of the parameters U_{fc} and U_{ff}. This is in contrast to Liu and Ho,[76] who assume that the dynamics of the f-d screening leads to the major effect in the valence spectrum.

In view of these simplifications better agreement cannot actually be expected but the degree of agreement found in all the spectroscopies does indicate that the major effects have been included in the model calculations. We again emphasize the philosophy given earlier[22,23,27] that one should use values for $c(f^0)$ and Δ from electron spectroscopy mainly as a guideline for future experiments and theoretical treatments of Ce and its compounds.

The separation between f^1 and f^2 final states is related to $\epsilon_f + U$. In order to obtain a separation similar to the one experimentally observed, we had to use values for U smaller than those required for the XPS data. Herbst *et al.*[62] have calculated U for Ce, and found 5 eV which compares well with the range of 4.5—5.5 eV we found in BIS. For XPS, U was in the range 5.5—7.5 eV.[23] The larger values for the XPS case can—at least partially—be explained by the presence of the $3d$ core hole, which will contract the outer levels and thereby increase U. These arguments emphasize the possible importance of the first point above.

We would like to draw attention to the shifts of the La f^1 and Ce f^2 BIS peaks as a function of alloying (Table I). At first glance one might correlate the values of ϵ_f with the position of the f^1 peak in, for instance, the Ce-Ni compounds. Qualitatively such a correlation is indeed in agreement with the trend of an increasing f^1 signal and the f^2 peak shift to higher energy. The XPS results do suggest, however, significant changes in Δ. Since the energy splitting between the f^1 and f^2 states depends somewhat on Δ it would be premature to derive exact values for the shift of ϵ_f from the shift of the BIS f^2 peak. Furthermore, we do not yet know the effect of the screening of the f^1 and f^2 states by the valence electrons on the peak separations.

The dominant contribution to the width of the f^2 peak is due to multiplet splitting.[43] In Fig. 7 we show the spectrum of $CeNi_2$ with a theoretical simulation including multiplet structure. The details of these simulations are

TABLE III. Comparison of $c(f^0)$ values derived from the relative peak intensities in BIS, $3d$ XPS, and $3d$ XAS.

	XPS[a]		BIS	XAS
Material	Δ (meV)	$c(f^0)$	$c(f^0)$	$c(f^0)$
Ce	30	<0.05	0.02—0.05	~ 0.04
Ce_7Ni_3	60	<0.05	0.02—0.08	
CeNi	70	~ 0.05	0.10—0.11	
$CeNi_2$	100	~ 0.12	0.25—0.23	~ 0.22
$CeNi_5$	70	~ 0.16	0.42—0.34	~ 0.18
$CeCo_2$	120	~ 0.18	0.42—0.29	
$CeCo_5$	110	~ 0.13	0.38—0.34	
$CeRu_2$	120	~ 0.20	0.40—0.28	
Ce_7Pd_3	30	<0.05	<0.07	
CePd	90	<0.05		<0.06
Ce_3Pd_5	120	<0.05	<0.07	<0.08
$CePd_3$	150	~ 0.10	0.08—0.08	<0.2
$CePt_3$	150	~ 0.14	0.14—0.15	
CeAu	25	<0.05	<0.07	<0.04
$CeSn_3$[b]	50	<0.05	<0.07	~ 0.04

[a] All from Ref. 23 except $CePt_3$.

[b] Reference 44.

given in the Appendix. The first conclusion to be drawn from Fig. 7, and similar comparisons made for other intermetallic compounds, is that the f^2 peak shape in Ce compounds is simulated quite well when the multiplet is taken into account, just as previously found for the pure metal.[43] The second point is that inclusion of the multiplet does not drastically change our estimate of the value of $c(f^0)$ from BIS. A value of 0.25 is appropriate to the curve in Fig. 7 and a value of 0.25 was derived using the same background subtraction and the curves of Fig. 5 which were calculated without multiplet effects. Consequently we have neglected multiplet splitting in determining the values for $c(f^0)$ given in Table III.

The model calculations have some difficulty reproducing the line shape of the f^1 peak near E_F, where theory predicts a peak about T_K, or ~ 0.1 eV, above E_F, as shown in Fig. 7, whereas experimentally we find a peak ~ 0.5—0.7 eV above E_F. Also, for those materials with unfilled transition-metal d states above E_F, such as $CeRu_2$, $CeCo_5$, and $CeCo_2$, even a 1 eV extra (noninstrumental) broadening did not simulate the experimental data well. We strongly suspect a non-Lorentzian contribution to the observed line shape not explicable by spin-orbit splitting of the $4f$ levels alone. The problem of the f^1 line shape deserves more attention than we can give it here, both in terms of experimental work and folds of different instrumental functions and potential unbroadened line shapes, as well as theoretical work on "fine tuning" of the model calculations. If the discrepancies are real then they have important ramifications for Kondo-type theories which predict a peak at E_F with width of the order of T_K/N_f. Ideally, studies of these effects should be accompanied by independent estimates of the $f_{5/2}$:$f_{7/2}$ ratio.

As a final point it is appropriate to discuss the term "mixed valence" as applied to Ce. This term was introduced mainly for Sm, Tm, and Yb compounds. It is commonly believed that the mixed-valence or configuration-fluctuation phenomena have the following (partially overlapping) characteristics.

(1) The f electrons are strongly correlated so that the Coulomb correlation energy is much larger than the f hybridization or bandwidth.

(2) The f level has a small hybridization Δ (of the order 0.01 eV) and its energy separation to the Fermi energy is of the same order as Δ.[77]

(3) The photoemission from the valence levels is dominated by the atomic multiplet structure with little distortion due to interaction with the conduction states. There is no observable dispersion of the f states.

(4) When an element has mixed-valence compounds then the variation of f-electron counts that can be found in compounds of that element is approximately 1.

(5) In all cases of dynamic mixed valence in heavy rare-earth compounds there has never been a need to consider more than two configurations in the ground state. This is not the case for transition metals, for instance, where higher polarity states must sometimes be considered.[78,79]

We can now say that the spectroscopic properties of Ce and its intermetallic compounds lead to a picture of the Ce $4f$ levels, which is rather different from the above. Clearly, U is still larger than Δ, but the more relevant parameter $N_f\Delta$ ranges up to 2 eV. The bare f level is apparently at least 1 eV below E_F in most cases, as evidenced by comparison of VB photoemission with model calculations. We do not expect strong dispersion effects in the contribution to VB photoemission driven by the f matrix elements, but the required angle-resolved single-crystal photoemission studies to clarify this point have not been done yet. The variation in f-electron count derived from BIS, XPS, and XAS of a very wide range of Ce compounds is only approximately 0.2 electrons, in contrast to Sm, Tm, or Yb. Finally the combination of spectroscopy with model calculations gives evidence for some mixing of f^2 character into the ground state. Numerically we arrive at $c(f^2)$ up to $\sim 5\%$, which is not much, but which significantly affects the intensity distributions found. Thus in almost all points Ce shows major differences to the so-called mixed-valence materials of the heavy rare earths. While it is clear that many Ce properties are closely related to the narrow-band phenomena of heavy rare earths, its spectroscopic properties are intermediate between the heavy rare earths and transition metals and alloys. Indeed, if one uses mixed valence as applied to heavy rare earths as a starting point one comes to many incorrect ideas about the spectra, such as peak intensities being directly related to ground-state occupation numbers, absence of structure in valence-band PS due to hybridization with the conduction band, and BIS peak positions being independent of hybridization. It is not for us to argue for or against the use of the term mixed valence to describe the properties of Ce and its compounds, but the above considerations clearly point out significant differences between the "narrow-band" and mixed-valence phenomena in Ce and the heavier rare earths.

V. CONCLUSIONS

A comparison of the BIS data with theory shows that just as in photoemission and XAS the intensity of the low-energy region (relative to E_F) is considerably larger than that expected in a static model. The transfer of weight to the low-energy region depends strongly on the hybridization between the f level and the conduction states, which is already known from XPS to be considerable.[17,23,36] The BIS data presented give strong support for the theoretical framework used and the conclusion that the f-electron count in Ce intermetallic compounds varies less than previously thought. Small discrepancies observed in a detailed comparison of f-electron counts obtained from XPS and BIS and the BIS linewidths are probably a result of some necessary approximations in the calculations and point to the direction that further work should take. In general the hybridization of the Ce f level and the $c(f^0)$ are larger for those compounds in which the f electron does not exhibit normal localized magnetic behavior (e.g., $CeNi_2$, $CeNi_5$, $CeRu_2$, $CeCo_2$). We believe that the hybridization is the driving force for loss of the local magnetic moment, and not changes in the f-electron count, which are confirmed by the BIS studies to be rather small. Experimentally, the most pressing need is to extend spectroscopic studies to Ce or $CeTh_x$ at low temperatures, where again there is no localized f-electron moment, and to dilute Ce alloys where larger changes in f-electron count may be observable.[80]

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APPENDIX

This appendix describes our approach to the separation of the f^1 and f^2 peaks and to multiplet effects in the spectrum. The major difficulty in assessment of the intensities arises from the background and contributions of the other unoccupied states and/or inelastic losses which are all poorly understood at present. If we compare the La-Ni and Ce-Ni spectra in Figs. 1 and 2 it seems a fairly good approximation to describe the background as a step function, with the f signal superimposed on it, as indicated in the upper part of Fig. 6 for Ce. The relative intensities of the two peaks estimated with this background are listed as the first number in the experimental $I(f^1)$ peak intensities in Table II.

Another solution to the problem of the background in Ce BIS spectra is given by a "calibration" of the shape of the corresponding La spectrum, where the f^1 peak clearly sits on a (usually) simple background as shown in the lower part of Fig. 6. In La it is easy to estimate the ratio of f electron derived intensity to the other intensity. Assuming Scofield's f-electron cross sections[81] and a drop in degeneracy from 14 to 13 in Ce, we can estimate the f contribution in Ce to be $\frac{4}{3}$ that of La.[47] We then draw a background for the Ce compound resembling that of the La analog, with its intensity normalized to give the correct ratio of f-electron-derived intensity to background or non-f intensity. The result is illustrated in the middle panel of Fig. 6, and the relative f^0 intensities derived by this method are given as the second numbers in the experimental $I(f^1)$ column of Table II. This procedure slightly increases small $I(f^1)$ values and slightly lowers larger $I(f^1)$ values.

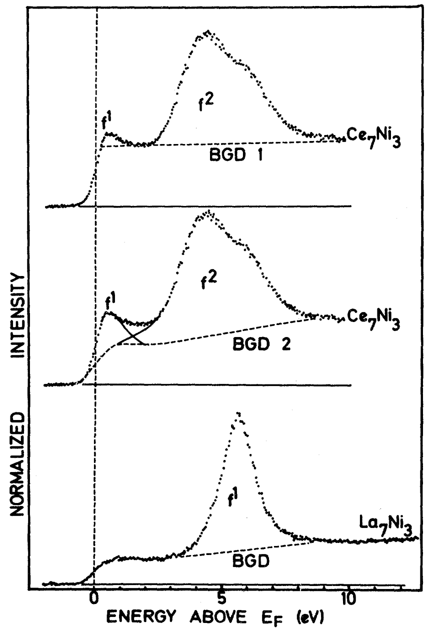

FIG. 6. BIS of Ce-Ni$_3$ with two different background subtraction procedures as described in text.

Another point to be considered is the f^2 multiplet. For the calculated spectrum in Fig. 7 we included the full f^2 multiplet effect. The purposes of the calculation are as follows.

(1) To check that the calculations could reproduce the observed line shapes if the full multiplet structure was included.

(2) To check that neglect of the multiplet structure in the calculation used for Fig. 5 did not lead to serious changes in the value of $c(f^0)$ derived from BIS.

(3) To identify the presence of any unexpected broadening of the spectra.

The results of a calculation for CeNi$_2$ are presented in Fig. 7. There is a discrepancy in the f^2 peak positions which may be partly due to difficulty in locating E_F exactly in the experimental spectrum, but could also be related to other effects. A constant background has been subtracted from the experimental spectrum by the method outlined in the top panel of Fig. 6. We assumed that the splittings ϵ_i and weights of the f^2 lines are the same as deduced by others.[42,43] This is justified because most of the experimental f^2 peaks show rather similar shapes (see also the energies for the peaks and shoulders of the f^2's in Table I). The splittings were simulated by calculating spectra with $U=U_0+\epsilon_i$ and adding the spectra with the weights w_i. The calculation leads to a larger width of the total f^2 intensity, because the f^2 intensity is made up of several peaks separated approximately (exactly if it were not for ΔE) by ϵ_i. A semielliptical band of width 3.75 eV

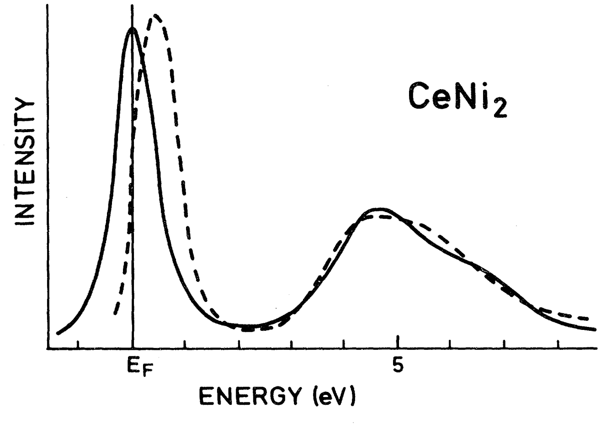

FIG. 7. Experimental BIS of CeNi$_2$ (dashed line) as compared to the calculated spectrum including simulated multiplet effects. The multiplet structure was approximated by lines at $\epsilon_i=0$, 0.54, 0.95, 1, 8, and 2.27 eV, with weights of 0.39, 0.26, 0.10, 0.06, and 0.19 (see Ref. 42); then five BIS spectra were calculated with $U=U_0+\epsilon_i$, Δ as from XPS, and added with the appropriate weights. U_0 was 5.4 eV (5.5 eV in XPS).

was used to simulate the Ni *d* bands, as described in more detail in Refs. 34—36. A Gaussian broadening of 0.65 eV was applied to account for the instrumental resolution. To reproduce the experimental widths an energy-dependent Lorentzian broadening of the form $2\Gamma(\epsilon)=2\Gamma_0+2\Gamma_\epsilon(\epsilon-E_F)$ was introduced with $2\Gamma_0=0.5$ eV, $2\Gamma_\epsilon=0.2$ eV for $CeNi_2$. We expect the lifetime broadening to rise approximately linearly with energy, thus the energy-dependent part of $\Gamma(\epsilon)$ may be ascribed to lifetime broadening. The broadening at E_F given by $2\Gamma_0$ is not fully understood but at least part of it is due to the spin-orbit splitting of 0.25 eV (see also discussion in Refs. 42 and 43).

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[56] f^3 final states do not play a significant role. The intensity is rather low and they are higher in energy than the f^2 state by $2U$ which must lead to a larger lifetime broadening.

[57] The $CePt_2$ we prepared was too brittle and air sensitive for use in XPS experiments. We decided to try to prepare $CePt_3$ as UPt_3 exists, and the compounds with higher transition-metal content are normally more stable. We expected to find either a new compound or a two-phase material with $CePt_2$ and Pt. However, the x-ray diffractogram showed only the lines of $CePt_2$ with a small change in lattice constant. We cannot be certain that the $CePt_3$ material is a single phase, but the results should show the tendency of the interactions between Ce and Pt. Note also M. M. Abd-Elmeguid *et al.* [Solid State Commun. **36**, 69 (1980)] found a single $EuPt_2$-like phase up to $EuPt_{3.3}$.

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[64] Note that $\Phi(f^n)$ looks similar to an atomic configuration, which is not what we wish to imply as the models used in this paper involve the $5d6s$ bands and local $4f$ configurations (Refs. 34—36). A more precise choice of the wave function is

$$\psi = \sum_l \alpha_l^0 f^0 \Psi_i^N + \sum_k \alpha_k^1 f^1 \Psi_k^{N-1} + \sum_l \alpha_j^2 f^2 \Phi_j^{N-2} ,$$

where the Φ_i^m are the band electron states containing m electrons and i labels an m electron basis set. The weights of the f^n components are then given by

$$c(f^n) = \sum_i (\alpha_i^n)^2 .$$

[65] Note that our ϵ_f is essentially identical to the Δ_- of Herbst *et al.* which is defined as a many-electron ionization potential for the f electrons, i.e., an ionization potential including most relaxation and screening effects.

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