

Occupancy and hybridization of the f level in Ce compounds

O. Gunnarsson

Max-Planck Institut für Festkörperforschung, D-7000 Stuttgart 80, Federal Republic of Germany

K. Schönhammer

I Institut für Theoretische Physik, Universität Hamburg, D-2000 Hamburg, Federal Republic of Germany

J. C. Fuggle and F. U. Hillebrecht

Institut für Festkörperforschung, Kernforschungsanlage Jülich, D-5170 Jülich, Federal Republic of Germany

J.-M. Esteve and R. C. Karnatak

Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, Bâtiment 209c, F-91405 Orsay Cedex, France, and Université de Paris-Sud, Bâtiment 350, F-91405 Orsay Cedex, France

B. Hillebrand

Research Laboratories of Siemens AG, Abt. FLMET1, 8520 Erlangen, Federal Republic of Germany

(Received 8 August 1983)

We compare experimental and theoretical core-level and valence photoemission, bremsstrahlung isochromat, and $3d \rightarrow 4f$ x-ray absorption spectra as well as susceptibility data for Ce compounds. Using the Anderson impurity model and one set of parameters, we obtain an essentially consistent description of these experiments. We deduce new values for the occupancy of the f level and its coupling to the conduction states. These values are substantially larger than the traditional ones.

Ce and its compounds have many anomalous properties, for which no quantitative (or sometimes even qualitative) description exists.¹⁻³ Similar effects are also observed in uranium compounds.³ These properties are related to the intermediate character of the Ce $4f$ (and U $5f$) electrons, which show both localized and delocalized behavior. The discussion has often centered on the population n_f of the f level and its coupling Δ to the conduction states. The purpose of this paper is to report new results for n_f and Δ from a quantitative comparison of theoretical and experimental core-level, valence-band, and $3d \rightarrow 4f$ x-ray absorption spectra (XAS) as well as susceptibility data. The new values are substantially larger than the traditionally accepted ones.

Thermodynamic, transport, and neutron scattering data have led to estimates of $\Delta \sim 0.01$ eV.¹⁻⁴ Values for n_f have usually been obtained from lattice parameter data, and $n_f = 0.55$ has, for instance, been quoted for CePd₃.¹ CeRu₂, CeNi₂, and CeNi₃ have often been assumed to have $n_f = 0$,⁵ but $n_f = 0.4$ has also been proposed for CeRu₂.¹ Our new values are not entirely without precedent, however, since Compton scattering,⁶ core,⁷ valence,⁸ and L_3 x-ray absorption⁹ spectra suggested that both n_f and Δ could be larger in Ce intermetallics than generally assumed.¹⁰

Ce compounds are often described in an Anderson impurity model,

$$H = \sum_{k,\sigma} \epsilon_k n_{k\sigma} + \sum_{m,\sigma} \epsilon_f n_{m\sigma} + \sum_{k,m,\sigma} (V_{km} \psi_{k\sigma}^\dagger \psi_{m\sigma} + \text{H.c.}) + U \sum_{m,\sigma} n_{m\sigma} n_{m'\sigma'} + \epsilon_c n_c - (1 - n_c) U_{fc} \sum_{m,\sigma} n_{m\sigma}, \quad (1)$$

where ϵ_f is the (bare) energy of the f level, with orbital (m) and spin (σ) degeneracies, ϵ_k is the energy of a conduction state, and V_{km} is a hopping matrix element between these states. The core level is described by ϵ_c , U is the effective f - f Coulomb interaction, and U_{fc} is the core-hole- f -electron interaction. We use the model assumption¹¹

$$\pi \sum_k V_{km}^* V_{km'} \delta(\epsilon - \epsilon_k) = \pi \sum_k |V_k|^2 \delta(\epsilon - \epsilon_k) \delta_{mm'} \equiv F(\epsilon) \delta_{mm'}, \quad (2)$$

We estimate $F(\epsilon)$ from valence photoemission and define Δ as the average of $F(\epsilon)$ over the occupied part of the conduction band.

We have developed a theory¹² for the core, valence, and $3d \rightarrow 4f$ x-ray absorption spectra, taking advantage of an idea of Ramakrishnan¹³ and Anderson,¹⁴ who pointed out that the model (1) has a small parameter, N_f^{-1} , where N_f is the degeneracy of the f level. Our method provides quite accurate spectra for $N_f \geq 6$, and for $N_f \rightarrow \infty$ ($N_f \Delta = \text{constant}$), the method is exact.

In Fig. 1 we show $3d$ core spectra for CeRu₂.¹⁵ The peaks are classified according to the number of f electrons in the corresponding final states. The weight of the f^2 shoulder depends sensitively on Δ , and the weight of the f^0 peak tracks $1 - n_f$. The experimental curve is well reproduced for $n_f = 0.85$ and $\Delta = 0.10$ eV, while $n_f = 0.54$ gives too much weight for the f^0 peak and $\Delta = 0.05$ eV leads to a very weak f^2 shoulder. Due to the neglect of multiplet effects the calculated f^1 peak is somewhat too narrow.

Figure 2 shows the valence spectrum of CeRu₂. The experimental spectrum⁸ was obtained at the resonance photon energy (122 eV), where the f emission is enhanced. Since the spectrum off resonance (e.g., 115 eV) is fairly flat,⁸ we have not tried to subtract the conduction-band emission, which is not included in the theory. The parameters obtained from the core spectrum give a reasonable description of the valence spectrum. The deviation around -2 and -3 eV could be due to the conduction-band emission.

It is controversial whether the peak close to the Fermi energy, ϵ_f , in many Ce compounds is due to f or d emission,^{8,16} where f emission is the intensity proportional to

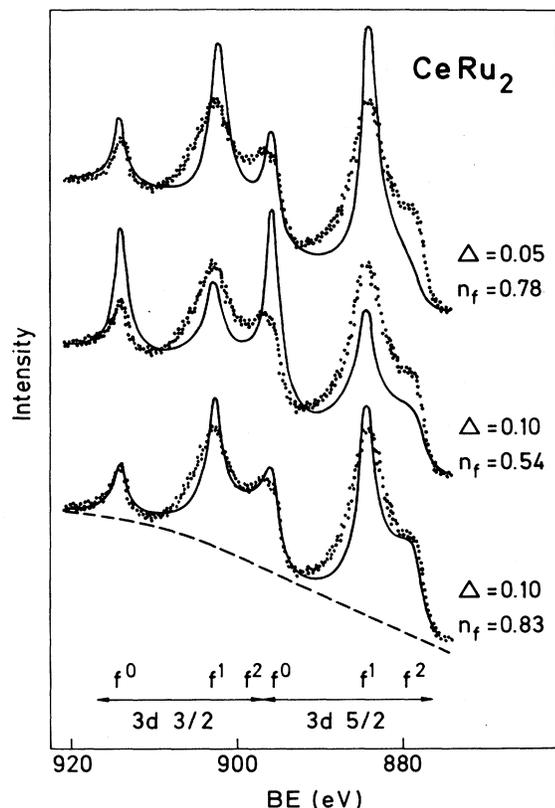


FIG. 1. The core spectrum for CeRu_2 according to experiment (dots) and theory (full curve). To describe the spin-orbit splitting of the $3d$ level, we have superimposed two calculated spectra with the appropriate energy separation and weights. We have also added an inelastic background (broken curve) and used a (Lorentzian) broadening of 1.8 eV [full width at half maximum (FWHM)]. The value of n_f is varied by changing ϵ_f . BE stands for binding energy.

the square of the f -level dipole matrix element. We find that the f emission always shows a peak at ϵ_F with some intensity,¹² corresponding to transitions to final states where a conduction electron close to ϵ_F has been removed. The emission at higher binding energies corresponds to final states, where configurations with an f electron have a smaller weight. The parameters from the core spectrum lead to a

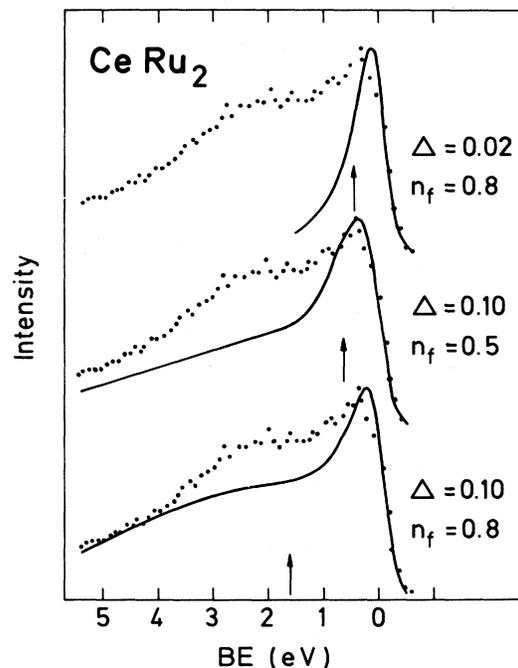


FIG. 2. The valence spectrum of CeRu_2 . For the lower theoretical curve the same parameters as for the lower curve in Fig. 1 were used, and the other curves were obtained for the values of n_f and Δ indicated. We used a Gaussian broadening of 0.47 eV (FWHM). The experimental spectrum is due to Allen *et al.* (Ref. 8).

weight of the peak at ϵ_F which is comparable to the experimental weight,¹⁷ strongly suggesting that for CeRu_2 this peak has a large f character. Interference between f and d emission is not included here. This effect in particular influences the peak at ϵ_F , and could lead to a different photon-energy dependence for this peak than for the rest of the f emission.

We have also calculated the $3d \rightarrow 4f$ x-ray absorption and the bremsstrahlung isochromat spectra (BIS), using the value of Δ determined from x-ray photoemission spectroscopy (XPS). The value of n_f was varied to obtain good agreement with experiment. We have performed similar calculations for CePd_3 , CeNi_2 , and CeNi_5 , and Table I sum-

TABLE I. The f -level hybridization Δ and the f occupancy n_f as deduced from the core-level photoemission (XPS), the $3d4f$ absorption (XAS), and the bremsstrahlung isochromat spectra (BIS) and the static, $T=0$ susceptibility (χ) (Ref. 18). "Traditional" estimates of n_f correspond to $n_f=0$ for CeRu_2 , CeNi_2 , and CeNi_5 and $n_f=0.5$ for CePd_3 .

	Δ (eV)		n_f		
	XPS	XPS	3d XAS	BIS	χ
CeRu_2	0.10	0.83		~ 0.7	0.78
CePd_3	0.11	0.91	0.86	0.97	0.82
CeNi_2	0.10	0.84	0.79	0.78	0.74
CeNi_5	0.09	0.79	0.81	~ 0.8	

marizes the parameters found. Due to the large background, the importance of multiplet effects and the neglect of d - f interference, we expect the values of n_f deduced from BIS to be less reliable than the other results. The description of experiment requires $U \sim 6$ – 7 eV and $U_{fc} \sim 10$ – 11 eV, in fair agreement with the *ab initio* estimates¹⁹ $U = 5$ eV and $U_{fc} = 10.3$ eV. The small differences between the parameters deduced from different experiments may be due to the simplicity of the model and to uncertainties in the fit procedure and the experimental data. The experiments also have different surface sensitivities and are performed at different temperatures.

We now discuss how some previous estimates of n_f and Δ can be rationalized within the framework of our new parameters. Values of $\Delta \sim 0.01$ eV have been obtained⁴ from the static, $T = 0$ susceptibility χ . The susceptibility has been calculated^{11,13} to lowest order in $1/N_f$ for $U \rightarrow \infty$. For a constant $F(\epsilon)$ and a broad band, we obtain

$$\chi \sim \frac{1}{\Delta} \frac{n_f^2}{(1-n_f)} \quad (3)$$

If the traditional small values of n_f are used, Eq. (3) requires a small Δ (say, $\Delta \sim 0.01$ eV) to explain the experimental χ . Such an estimate of Δ , however, depends dramatically on n_f , and the values of n_f in Table I lead to $\Delta \sim 0.1$ eV.²⁰ Since we now have estimates of Δ from the core spectra, we can use χ for the determination of n_f .²¹ Such estimates are shown in Table I. There are substantial uncertainties in both the experimental and the calculated f electron susceptibility. However, even a reduction by a factor of 2 of the experimental susceptibility or the estimated value of Δ would, for instance, only change the estimate of n_f for CeRu₂ by 0.09.

Also from the quasielastic peak width $\Gamma/2$ in neutron scattering data,²² small values of Δ have been inferred. Calculations of Kuramoto and Müller-Hartmann²³ suggest, however, that Δ is substantially larger than $\Gamma/2$ for the large values of n_f found here. Using a model with spin degeneracy ($N_f = 2$), Oh and Doiniach⁷ deduced $\Delta \sim 1$ eV for CePd₃

from the $3d$ core-level spectrum. In our calculation, which includes orbital degeneracy, Δ enters in the combinations $(N_f - 1)\Delta$ (f^2 peak) or $N_f\Delta$ (f^0 peak), explaining why their estimate of Δ is an order of magnitude larger than ours.

Small values of n_f have been obtained from the lattice parameter, L , assuming a linear relation²⁴ between L and n_f .¹ This assumption breaks down for large values of Δ , since the hopping between the f level and the conduction states can influence L substantially. If $n_f \approx 0$ or $n_f \approx L$, this effect is small, but for $n_f \sim 0.5$, hopping could lead to a reduction L comparable to the difference between the hypothetical three- and four-valent compounds.¹² The neglect of this nonlinear dependence of L on n_f causes an underestimate of n_f .

In conclusion, we have found that the Anderson impurity model with one set of new values for n_f and Δ can describe a large body of experimental data. The traditional values of Δ (~ 0.01 eV) are inconsistent with the core and valence spectra. The old estimates for n_f disagree with the core-level photoemission, the $3d \rightarrow 4f$ XAS, and the BIS spectra and, if we use the new values for Δ , the $T = 0$ susceptibility data. We hope this paper will stimulate further attempts to rationalize other experimental results of Ce compounds, in particular thermodynamic and transport data, in terms of the new values of n_f and Δ .

ACKNOWLEDGMENTS

We have benefited from discussions with numerous people, in particular J. W. Allen, M. Campagna, R. M. Martin, and J. W. Wilkins. We thank D. Wohlleben, H. Ludwigs, D. Scheitor, and P. Weidner for providing susceptibility data prior to publication. We are also grateful to the Laboratoire pour l'Utilisation du Rayonnement Electromagnétique technical staff for their valuable aid and to the Groupe Anneux du Laboratoire de l'Accélérateur Linéaire for their help in operating the equipment necessary for the XAS results.

- ¹J. M. Lawrence, P. S. Riseborough, and R. D. Parks, Rep. Prog. Phys. **44**, 1 (1981); in *Valence Instabilities*, edited by P. Wachter and H. Boppert (North-Holland, Amsterdam, 1982).
- ²*Valence Fluctuations in Solids*, edited by L. M. Falicov, W. Hanke, and M. B. Maple (North-Holland, Amsterdam, 1981).
- ³*Proceedings of the International Conference on the Physics of Actinides and Related 4f Materials* [Physica B **102** (1980)].
- ⁴D. M. Newns and A. C. Hewson, J. Phys. F **10**, 2429 (1980).
- ⁵A. Iandelli and A. Palenzona, in *Handbook on the Physics and Chemistry of Rare Earths*, edited by K. A. Gschneidner and L. Eyring (North-Holland, Amsterdam, 1979), Vol. II, p. 1.
- ⁶U. Kornstädt, R. Lässer, and B. Lengeler, Phys. Rev. B **21**, 1898 (1980).
- ⁷See, e.g., J. C. Fuggle, M. Campagna, Z. Zolnieriek, R. Lässer, and A. Platau, Phys. Rev. Lett. **45**, 1579 (1980); G. Krill, L. Abadli, M. F. Ravet, J. P. Kappler, and A. Meyer, J. Phys. (Paris) **41**, 1121 (1980); S.-J. Oh and S. Doiniach, Phys. Rev. B **26**, 2085 (1982).
- ⁸J. W. Allen, S.-J. Oh, I. Lindau, J. M. Lawrence, L. I. Johansson, and S. B. Hagström, Phys. Rev. Lett. **46**, 1100 (1981); M. Croft, J. H. Weaver, D. J. Peterman, and A. Franciosi, *ibid.* **46**, 1104 (1981); J. W. Allen, S.-J. Oh, I. Lindau, M. P. Maple, J. F. Suasuna, and S. B. Hagström, Phys. Rev. B **26**, 445 (1982); Y. Baer,

- H. R. Ott, J. C. Fuggle, and L. E. De Long, Phys. Rev. B **24**, 5384 (1981).
- ⁹K. R. Bauchspiess, W. Boksich, E. Holland-Moritz, H. Launois, R. Pott, and D. Wohlleben, Ref. 2, p. 417; G. Krill, J. P. Kappler, A. Meyer, L. Abadli, and M. F. Ravet, J. Phys. F **11**, 1713 (1981).
- ¹⁰B. Johansson, Philos. Mag. **30**, 469 (1974), however, deduced from thermodynamic data that n_f is close to one in Ce.
- ¹¹A. Bringer and H. Lustfeld, Z. Phys. B **28**, 213 (1977).
- ¹²O. Gunnarsson and K. Schönhammer, Phys. Rev. Lett. **50**, 604 (1983); Phys. Rev. B (to be published).
- ¹³T. V. Ramakrishnan, Ref. 2, p. 13; T. V. Ramakrishnan and K. Sur, Phys. Rev. B **26**, 1798 (1982).
- ¹⁴P. W. Anderson, Ref. 2, p. 451.
- ¹⁵For CeRu₂ we used

$$F(\epsilon) = 2V^2(B^2 - \epsilon^2)^{1/2}/B^2$$

for $-6 \leq \epsilon \leq 0.6$ and

$$F(\epsilon) = 2V^2(B^2 - \epsilon^2)^{1/2}/B^{2*}(0.6 - 2\epsilon)/1.8$$

for $0.6 \leq \epsilon \leq 0$ with $B = 6$ and $\epsilon_F = 0$. For CePd₃ we assumed

$$F(\epsilon) = 0.33V^2(6 + \epsilon)$$

for $-6 \leq \epsilon \leq -3$,

$$F(\epsilon) = V^2[0.99 - (\epsilon + 1.8)(\epsilon + 3)/3]$$

for $-3 \leq \epsilon \leq -1.8$, and

$$F(\epsilon) = V^2(0.22 - 0.428\epsilon)$$

for $-1.8 \leq \epsilon \leq 0$. A semielliptic form

$$F(\epsilon) = 2V^2[B^2 - (\epsilon - \epsilon_0)^2]^{1/2}/B^2$$

was used for CeNi₂ and CeNi₅. The parameters $\epsilon_0 = -1.995$ eV, $B = 2.005$ eV (CeNi₂), and $\epsilon_0 = -1.215$ eV, $B = 2.785$ eV (CeNi₅) were used.

¹⁶A. Franciosi, J. H. Weaver, N. Mårtensson, and M. Croft, Phys. Rev. B **24**, 3651 (1981); N. Mårtensson, B. Reihl, and R. D. Parks, Solid State Commun. **41**, 573 (1982); W. Gudat, M. Iwan, R. Pinchaux, and F. Hulliger, Ref. 1, p. 249.

¹⁷This peak is *not* due to the structure in $F(\epsilon)$ at $\epsilon = \epsilon_F$. The use of $F(\epsilon) = 2V^2(B^2 - \epsilon^2)^{1/2}/B^2$ for all $\epsilon \leq B$ only changed the peak at ϵ_F slightly.

¹⁸In another publication [J. C. Fuggle, F. U. Hillebrecht, Z. Zolnieriek, R. Lässer, Ch. Freiburg, O. Gunnarsson, and K. Schönhammer, Phys. Rev. B **27**, 7330 (1983)] we have given slightly different values for $w(f^0)$ and Δ , due to simplifications in the definition of Δ , the form for $F(\epsilon)$, and data analysis. We

have used the susceptibility data 1.47×10^{-3} (CePd₃), 0.67×10^{-3} (CeRu₂), and 0.83×10^{-3} (CeNi₂) emu/mole, which are obtained from K. H. J. Buschow, Rep. Prog. Phys. **40**, 1179 (1979); **42**, 1373 (1979); G. L. Olcese, J. Phys. (Paris) Colloq. **40**, C5-334 (1979); Ref. 4; and D. Wohlleben (private communication). We have not subtracted the contribution to χ from the conduction and core electrons due to the uncertainty in this procedure. Although this correction can be large, it should not influence our estimates of n_f very much.

¹⁹J. F. Herbst, R. E. Watson, and J. W. Wilkins, Phys. Rev. **17**, 3089 (1978); J. F. Herbst and J. W. Wilkins, Phys. Rev. Lett. **43**, 1760 (1979).

²⁰While the core spectroscopies depend primarily on the average value of $F(\epsilon)$ and less on its shape; the susceptibility centers mainly on $F(\epsilon)$ rather close to ϵ_F . If $F(\epsilon) \equiv \Delta$ is a constant we then need $\Delta \sim 0.05$ for CePd₃ to reproduce the χ and n_f calculated for the $F(\epsilon)$ in Ref. 15.

²¹To calculate the susceptibility, we have introduced spin-orbit splitting in the model (1) and used the $F(\epsilon)$ of Ref. 15.

²²E. Holland-Moritz, M. Lowenhaupt, W. Schmatz, and D. K. Wohlleben, Phys. Rev. Lett. **38**, 983 (1977).

²³Y. Kuramoto and E. Müller-Hartmann, Ref. 2, p. 139.

²⁴Evidence for a nonlinear relation between L and n_f has been given by G. Neumann, R. Pott, J. Röhler, W. Schlabit, D. Wohlleben, and H. Zahel, Ref. 1, p. 87 for some other rare-earth compounds.