Study of some Ce intermetallics by core-level photoemission

Study of some Ce intermetallics by core-level photoemission

R K Singhal†, N L Saini‡||, K B Garg†, J Kanski‡, L Ilver‡, P O Nilsson‡, Ravi Kumar§ and L C Gupta§

† Department of Physics, University of Rajasthan, Jaipur-302 004, India
‡ Department of Physics, Chalmers University of Technology, S-412 96 Göteborg, Sweden
§ Tata Institute of Fundamental Research, Bombay-400 005, India

Abstract. Ce intermetallics CeAlNi, CeAlCu and $CeNi_2Si_2$ have been studied by core-level photoemission spectroscopy to investigate their electronic structure. The Ce 3d XPS data clearly indicate that the final state is a quantum mechanical admixture of $4f^0$, $4f^1$ and $4f^2$ configurations in these systems with an increasing $4f^0$ contribution as Cu is replaced by Ni. The two Ni-based systems are found to be mixed-valence systems with $n_f < 1$ while the ground state of the Cu-containing system appears to retain a purely trivalent character with $n_f \simeq 1$. These results are in agreement with our earlier reported x-ray absorption and resonant photoemission data. The present study highlights the fact that the replacing of Ni by Cu seems to be propitious for driving the Ce from an intermediate-valence (IV) to a non-IV ground state. The results of Ce 3d and Ce 4d XPS are discussed.

1. Introduction

In cerium and actinide compounds, the hydridization of the f electrons with the conduction band gives rise to various kinds of interesting phenomenon. A great deal of scientific effort has been focused on the Ce 4f problem because of the diverse properties and elusive role of the 4f electrons. Ce compounds and intermetallics are distinguished for exhibiting a variety of interesting and most peculiar phenomena such as an intermediate valence (IV), a Kondo lattice, heavy-fermion superconductivity and magnetism, raising questions about the nature of their ground-state electronic configuration.

Some Ce-based intermetallics exhibit IV behaviour which cannot be reconciled within the framework of the Anderson impurity model. While the 4f states in the IV systems of heavy rare earths retain their atomic character as they have a very small 4f band width (about 0.1 eV), other Ce systems have been found to exhibit a more delocalized behaviour where the 4f band width can be as large as 1 eV and hence the 4f wavefunction can mix with the extended states of the solid. It is interesting that the 4f state appears localized in some compounds and delocalized in others, e.g. localized in hydrides and chalcogenides, slightly delocalized in the pnictides and more band like in some intermetallics. Understanding of this ambivalent and complex character continues to be elusive and represents a major challenge to solid state physicists.

In the evolution of the study of the properties of the 4f electrons in Ce and its compounds, photoemission spectroscopy has played a key role [1–16]. The intent of these investigations has been to identify the binding energy of the 4f states, their width, the degree to which

|| Permanent address: Department of Physics, University of Rajasthan, Jaipur-302 004, India.

they do or do not hybridize with other states and the relationship between the spectroscopic information and the ground-state properties. In principle, hybridization of the 4f levels in Ce could be inferred from measurements of the 4f level widths in photoemission from the valence bands. In practice, the width of the f band is small so that some resolution problems occur. In addition, the lifetime broadening and surface effects further complicate the matter [7, 8, 14–16]. The core-level photoemission line shapes have been widely used to diagnose hybridization of the 4f levels in Ce systems [9, 13–16]. The use of core-level line shapes is based on the concept that for a Ce atom, which has one 4f electron in the ground state, the lowest energy in a core ionized state is obtained when the core hole is screened by an extra 4f electron. The states with and without occupation of this screening state are termed 'well screened' or 'poorly screened'. The probability of occupation of this screening state will depend on the coupling of the other occupied states. This coupling is described in terms of *the degree of hybridization. If this degree of hybridization is small, then the probability of* electron transfer to this screening state is also small. The x-ray photoelectron spectroscopy (XPS) of Ce core levels for studies of screening effects is restricted to the 3d and 4d levels. The strong Coulomb interaction between the 4f and 4d levels gives rise to complicated multiplets in the 4d x-ray photoelectron spectra which are therefore not easy to analyse. The Ce 3d spectra show two sets of lines ($3d_{3/2}$ and $3d_{5/2}$ doublets) which correspond to poorly screened (f^1) and well screened (f^2) states. In addition, Ce also shows a $4f^0$ peak which is related to partial emptying of the 4f level and is attributed to the mixed-valence character of Ce [8, 13–16].

Ce intermetallics CeM_2Si_2 (M $\equiv$ transition metal) have been the focus of many experimental studies as the various properties of Ce vary with M to give a heavy-fermion superconducting system (with M $\equiv$ Cu) [17], IV systems (with M $\equiv$ Fe, Co, Ni, etc) [18, 19] and magnetically ordered systems (with M $\equiv$ Au, Cd, Ag) [20]. In the present study, we have investigated three interesting Ce intermetallic compounds, namely $CeNi_2Si_2$, CeAlNi and CeAlCu, using core-level XPS to study the valence state of Ce and the properties (i.e. localization, etc) of the 4f electron states. Earlier XANES and RESPES studies have shown that CeAlNi is a mixed-valence system, while the XAS spectrum of CeAlCu looks almost identical with that of heavy-fermion system with a purely trivalent ground state [21].

2. Experimental details

The samples were prepared by arc melting high-purity metallic constituents (about 99.9% purity) in an inert gas (Ar) atmosphere. The samples (button shaped) were melted repeatedly (five to six times) in the same atmosphere to ensure homogeneity. The weight losses of the final buttons were found to be less than about 1%. The resulting buttons were then wrapped in Ta foils and sealed in a quartz tube under vacuum. These samples were annealed in a standard manner at about 900 °C for 15 d to reduce the concentration of peritectic precipitates. The phase purity of the samples was checked by x-ray diffraction where about 5–10% impurity phases ($CeAl_3$, etc) were found in the CeAlCu sample. The other samples, CeAlNi and $CeNi_2Si_2$, were found to be single phase.

The XPS measurements were made in a Vacuum Generators ADES 400 system. Unmonochromated Al Kα x-rays were used to excite the spectra. The pressure in the ultrahigh-vacuum chamber was about 5×10^{-11} Torr during the measurements. The spectra were recorded with a total energy resolution of about 1 eV. Clean surfaces were obtained by argon ion bombardment. The high oxygen affinity of all the rare earths is well known and rapid oxide layer formation on the surface is very common. In order

to remove the surface contamination, the samples were sputtered with an argon ion beam (about 3 keV). The surface contamination was monitored by both O 1s XPS and the O signal in ultraviolet photoelectron spectra at about 6 eV. During the measurements, fast recontamination was observed. We noted this time effect by monitoring the O ultraviolet photoelectron spectroscopy (UPS) signal and found that we needed to resputter the samples after every 15 min. We did not observe the O 1s XPS signal after sputtering but still cannot rule out a small (about 5%) contamination as the O UPS signal could not be removed completely even after this routine sputtering. It is worthwhile mentioning that we did not find any signs of preferential sputtering and the relative intensities of the core levels were constant to within less than about 5%.

3. Results and discussion

Figure 1 shows the Ce 3d spectra of the compounds CeAlNi, CeNi$_2$Si$_2$ and CeAlCu. The spectra are normalized to the intensity of the most intense peak at about 884 eV. The spectra show two main peaks, corresponding to the 3d$_{5/2}$ and 3d$_{3/2}$ spin–orbit components. These main peaks are associated with the poorly screened 3d^{9}f^1 final state. Two additional sets of lines can be clearly seen in the spectra of CeAlNi and CeNi$_2$Si$_2$, labelled f^2 and f^0. These lines represent the Ce atoms in the 3d^{9}4f^2 and 3d^{9}4f^0 states, respectively. The energy separations between these lines are

$$E(f^0) - E(f^1) \simeq 12 \text{ eV} \qquad E(f^1) - E(f^2) \simeq 2\text{–}4 \text{ eV}.$$

The presence of these three sets of lines in x-ray photoelectron spectra may be attributed to the coexistence of the different configurations in the ground state of Ce. However, a significant contribution from the final state effects such as shake-up or shake-down, core hole screening, etc, cannot be ruled out and may be so pronounced as to mask completely the initial state in some cases.

The f^0 peak suggests that the Ce atoms are in the 4+ valence state while the 'well screened' f^2 peak indicates hybridization of the 4f levels and overlap of the 4f level with other orbitals [13–16]. Therefore the intensity of the f^0, f^1 and f^2 peaks provides qualitative information about the valence state (i.e. f counts) of Ce and hybridization of the 4f levels with the conduction band [8, 10, 13, 15, 16]. To address the problem of hybridization and valency in detail we have applied a deconvolution procedure [22]. The deconvoluted spectra of different samples are shown in figures 2–4 together with the fitted spectra. The fitted energy positions together with the fitting parameters used have been summarized in table 1.

Table 1. Ce 3d XPS peak binding energies (fitted) of Ce intermetallic compounds with respect to E_F. The energy values correspond to 3d$_{3/2}$. The spin–orbit coupling is about 18.5 eV and the branching ratio is 1.5 eV. The accuracy in measurements is 0.5 eV. The Gaussian widths Γ_G and Lorentzian widths Γ_L are also included in the table.

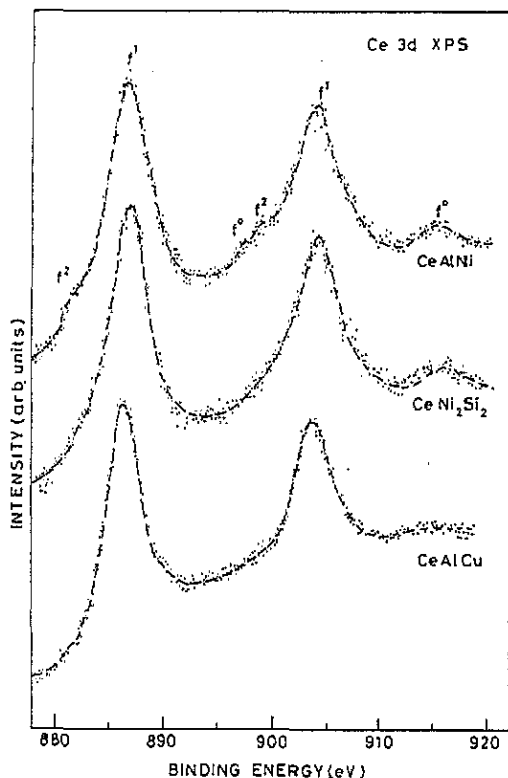| Compound | Peak binding energy (eV) | | | $E(f^0) - E(f^1)$ (eV) | Γ_G (eV) | Γ_L (eV) |
	f^0	f^1	f^2			
CeAlNi	915.2	903.2	901.1	12.0	3.00	1.16
CeNi$_2$Si$_2$	915.6	903.0	900.2	12.6	3.00	1.16
CeAlCu	914.4	902.4	901.4	12.0	3.00	1.16

Figure 1. Ce 3d x-ray photoelectron spectra of the intermetallics studied.
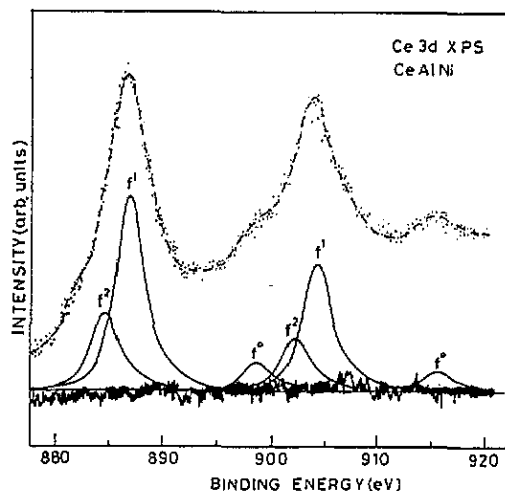
Figure 2. Deconvoluted Ce 3d x-ray photoelectron spectra of CeAlNi. Note the intensity of the f^0 peak.

Let us first discuss the results of the Ni-containing compounds, namely CeAlNi and CeNi$_2$Si$_2$. A significant intensity weight of the f^0 peak was found in the spectra of CeAlNi (figure 2) which is indicative of the mixed-valence nature of this compound. However, the intensity of the f^0 is slightly lower in the case of CeNi$_2$Si$_2$ (figure 3) which is also a known mixed-valence compound of Ce [21]. As discussed above, quantitative estimation of the valence is not possible from the XPS data, but we can say that Ce has, qualitatively speaking, a lower valence in CeNi$_2$Si$_2$ than in CeAlNi. This is also borne out from our x-ray absorption studies [21]. Before proceeding further it is worth noting that the 4d x-ray photoelectron spectra of these Ce compounds also contain evidence for the presence of different final states. Figures 5 and 6 show the Ce 4d spectra of CeAlNi and CeNi$_2$Si$_2$.

Although these cannot be interpreted in detail because of the strong 4d–4f interaction as mentioned earlier, some qualitative information can still be obtained. We have made an attempt to decompose the Ce 4d spectra into a few components suggested by the shapes of the raw spectrum. The spectra contain, of course, a large number of unresolved components due to multiplet interaction; so the present decomposition is only intended to emphasize the gross features. Each component cannot be associated with a single transition. The energy region between 105 and 115 eV also contains a contribution from Ni 3s emission. The peak at about 118 eV has been ascribed to the 4f^0 final states [8, 15] and can be seen clearly in the spectra of both compounds. The higher intensity of the 118 eV peak in the spectra of CeAlNi (figure 5) than in CeNi$_2$Si$_2$ is consistent with the higher valence of Ce in CeAlNi.
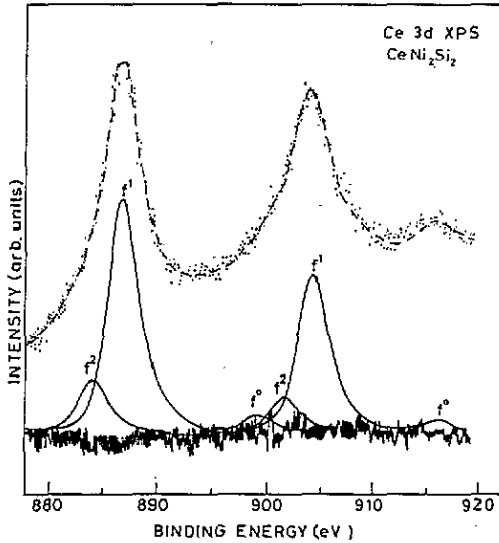
Figure 3. Deconvoluted Ce 3d x-ray photoelectron spectra of CeNi$_2$Si$_2$.
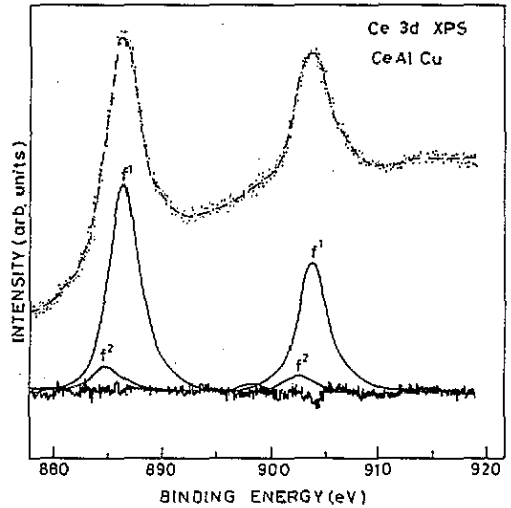
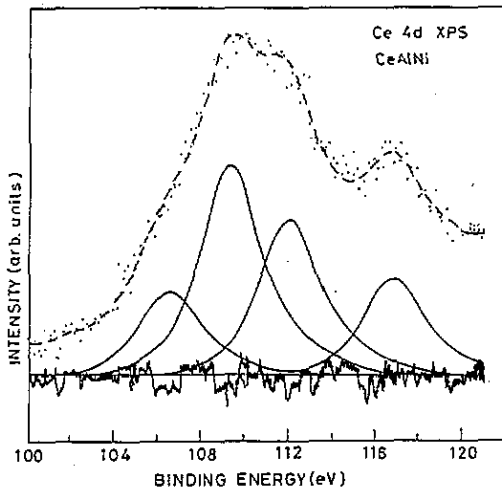**Figure 4.** Deconvoluted Ce 3d x-ray photoelectron spectra of CeAlCu. Note the negligible intensity of the f^0 peak.

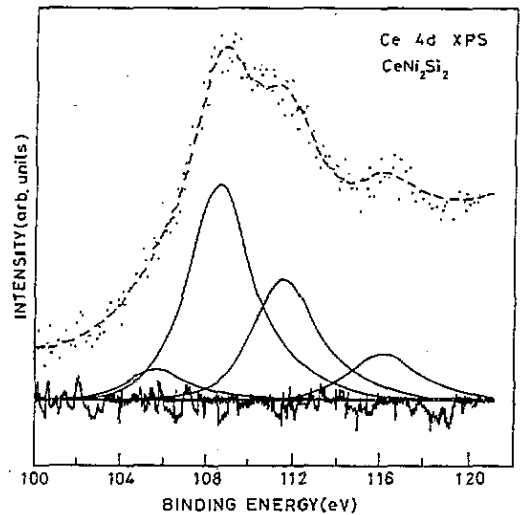**Figure 5.** Deconvoluted Ce 4d x-ray photoelectron spectra of CeAlNi.

Figure 6. Deconvoluted Ce 4d spectra of CeNi$_2$Si$_2$.

Now, we turn our attention to the spectra of the CeAlCu system. The deconvoluted Ce 3d spectra of this system are shown in figure 4 which look quite different from those of the Ni-containing mixed-valence compounds CeAlNi and CeNi$_2$Si$_2$ (figures 2 and 3). The spectral weight of the 3d^{9}4f^0 peak is negligible in the Ce 3d spectrum of CeAlCu. The intensity of the 3d^{9}4f^2 peak is also quite small. These results support the above assumption that the different configurations observed in the spectrum reflect the initial states as there

is no reason to expect significantly smaller final state interactions in CeAlCu than in other compounds. In figure 7 we also see that the 118 eV peak is quite small in this case. The intensities of the different final states of the three compounds are compared in table 2.
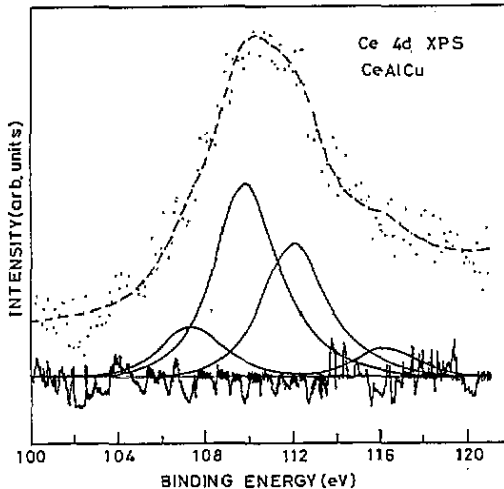

Figure 7. Deconvoluted Ce 4d spectra of CeAlCu.

Table 2. Relative intensities of the f^0, f^1 and f^2 peak final states in Ce 3d XPS. The intensities were estimated from the area of the respective peaks. The hybridization parameters Δ are also included in the table.

Compound	f^0:f^1:f^2	Δ (meV)
CeAlNi	0.10:0.64:0.26	140
CeNi$_2$Si$_2$	0.07:0.75:0.18	100
CeAlCu	0.03:0.86:0.11	45

It is well known that 4f levels in Ce and its compounds are less localized than in the heavier rare earths. However, it is not possible to determine the f counts from the core-level intensities of different peaks because of large initial as well as final state mixing of different configurations which has also been pointed out in earlier studies [8, 9, 13–16]. However, the ratio $r = I(f^2)/[I(f^1) + I(f^2)]$ has been reported to depend on Δ, the hybridization parameter [15]. Δ is defined as $\pi V^2 \rho_{max}$ where ρ_{max} is the maximum value of the density of conduction states and V is the hybridization matrix element. The Ce 3d spectra of CeAlNi (figure 2) show the distinct intensity of the $3d^9 4f^2$ peak and indicate a higher hybridization of the f levels. The spectra of CeNi$_2$Si$_2$ (figure 3) and CeAlCu (figure 4) also show a significant intensity of $4f^2$ peaks. Earlier core-level spectroscopy studies [15] have shown that the intensity of the $4f^2$ peaks increases with increasing Ni content in the CeNi$_x$ system *which, in turn, indicates increased hybridization. If we compare the spectra of CeAlNi and CeAlCu, we find the same trend as the substantially higher intensity of the f^2 peak is indicative of higher hybridization in the Ni-containing system.* In the Ce 3d spectra of CeNi$_2$Si$_2$, the f^2 peaks have more weight than in the Cu compound (CeAlCu) but a little less than that in the Ni compound (CeAlNi) despite its higher Ni content. This may be due to the different local structure of Ce in CeNi$_2$Si$_2$ as compared with CeAlNi and CeAlCu [21]. The hybridization parameter Δ is approximated from calculated correlation between Δ and

the well screened f^2 peak intensity, given by Fuggle *et al* [15]. We have also incorporated the approximate hybridization parameters Δ of the different compounds in table 2.

Finally, we would like to comment on the mixed-valence aspect of the Ce compounds studied here. On the basis of the above spectroscopic data it can be readily seen that the two Ni-based systems CeAlNi and CeNi$_2$Si$_2$ are mixed-valence systems while the copper-containing system shows no evidence of any mixed-valence behaviour, and Ce appears to retain a purely trivalent character. These findings are consistent with our earlier x-ray absorption and RESPES results [21]. Thus the present investigations, in conjunction with earlier studies, serve to show that Cu is very suitable for driving Ce intermetallics from an IV to a non-IV ground state. This behaviour may be attributed to the charge transfer in a rigid band picture where the 5d electrons are transferred to the 3d band of Ni from electro-negativity–affinity considerations [21,23]. This in turn lowers the E_F in these systems compared with the E_F of pure Ce and renders the hybridization favourable, driving Ce to a mixed-valence state where the Ce valence is more than 3+. On the other hand, when the 3d band is filled, no transfer is possible and Ce remains of a purely 3+ nature as in most Cu-containing systems (CeAlCu, in the present case). It is imperative to investigate whether the Cu system (CeAlCu) is a γ-type magnetic material or a new heavy-fermion system! In either case, some other measurements (specific heat, magnetic susceptibility, etc) are necessary to answer this question which may provide vital information about any heavy-fermion nature of this compound.

4. Conclusions

In conclusion, the electronic structures of CeAlNi, CeNi$_2$Si$_2$ and CeAlCu intermetallics have been investigated by core-level photoemission spectroscopy. The Ce 3d x-ray photoelectron spectra show three sets of lines corresponding to the $3d^9f^0$, $3d^9f^1$ and $3d^9f^2$ configurations. The $4f^0$ configuration indicates that Ce is in the 4+ valence state. Our XPS data indicate that the CeAlNi and CeNi$_2$Si$_2$ systems are mixed-valence systems where the f count is less than unity. On the other hand, the $3d^9f^0$ intensity in the 3d x-ray photoelectron spectra of CeAlCu is negligibly small and rules out the possibility that it is a mixed-valence system. We also conclude from the Ce 3d x-ray photoelectron spectra that the coupling of 4f levels with conduction states is quite different in Cu and Ni compounds. In CeAlNi, the 4f hybridization is stronger than in CeNi$_2$Si$_2$. 4f hybridization is found to be very small in CeAlCu. Because of the presence of the additional multiplets in the Ce 4d x-ray photoelectron spectra we have not drawn any quantitative conclusions from them. However, our deconvoluted spectra have encouraged us to make some qualitative comparison of the compounds studied. The conclusions of both the measurements (3d and 4d core-level XPS) agree qualitatively with each other.

References

[1]   Parks R D, Mårtensson N and Reihl B 1982 *Valence Instabilities* ed P Wachter and H Boppart (Amsterdam: North-Holland) p 239, and references therein
[2]   Kaskenmaki D C and Gschneidner K A Jr 1978 *Handbook on the Physics and Chemistry of the Rare Earths* ed K A Gschneidner Jr and L Eyring (Amsterdam: North-Holland) p 337
[3]   Allen J W, Oh S J, Lindau I, Lawrence J M, Johansson L I and Hagstrom S B M 1981 *Phys. Rev. Lett.* **46** 1100; 1982 *Phys. Rev.* B **26** 445
[4]   Mårtensson N 1985 *Z. Phys.* B **61** 457
[5]   Allen J W 1983 *J. Less-Common Met.* **93** 183
[6]   Hufner S 1992 *Z. Phys.* B **86** 241
[7]   Paparazzo E, Ingo G M and Zacchetti N 1991 *J. Vac. Sci. Technol.* A **9** 1416
[8]   Krill G, Kappler J P, Ravet M F, Amamou A and Meyer A 1980 *J. Phys. F: Met. Phys.* **10** 1031
       Krill G, Kappler J P, Meyer A, Abadli L and Ravet M F 1981 *J. Phys. F: Met. Phys.* **11** 1713
[9]   Fujimori A 1983 *Phys. Rev.* B **27** 3992
[10] Herbst J F and Wilkins J W 1979 *Phys. Rev. Lett.* **43** 1760
[11] Wertheim G K 1981 *Valence Fluctuations in Solids* ed L M Felicov, W Hanke and M B Maple (Amsterdam: North-Holland) p 67
[12] Patthey F, Imer J M, Schneider W D, Beck H, Baer Y and Delley B 1990 *Phys. Rev.* B **42** 8864
[13] Fujimori A 1983 *Phys. Rev.* B **28** 4489; 1983 *Phys. Rev.* B **28** 2281; 1985 *J. Magn. Magn. Mater.* 47–8 243
[14] Fuggle J C, Hillebrecht F U, Zolnierek Z, Freiburg Ch and Campagna M 1982 *Valence Instabilities* ed P Wachter and H Boppart (Amsterdam: North-Holland) p 267
[15] Fuggle J C, Hillebrecht F U, Zolnierek Z, Lasser R, Freiburg Ch, Gunnarsson O and Schonhammer K 1983 *Phys. Rev.* B **27** 7330
[16] Hillebrecht F U and Fuggle J C 1982 *Phys. Rev.* B **25** 3550
[17] Steglich F, Aarts J, Bredl C D, Leike W, Meschede D, Franz W and Schafer H 1979 *Phys. Rev. Lett.* **43** 1892
[18] Ammarguellat C, Escorne M, Krill G, Lapierre F, Haen P and Godart C 1987 *Phys. Status Solidi* b **143** 159
[19] Sampathkumaran E V, Kakowski G, Laubschat C, Kaindl G, Domke M, Schmiester G and Wortmann G 1985 *Valence Fluctuations* ed E Mullar-Hartmann, B Roden and D Wohlleben (Amsterdam: North-Holland) p 212
[20] Murgai V, Raaen S, Gupta L C and Parks R D 1982 *Valence Instabilities* ed P Wachter and H Boppart (Amsterdam: North-Holland) p 537
[21] Singhal R K 1990 *PhD Thesis* Rajasthan University
[22] Carley A F and Joyner R W 1979 *J. Electron Spectrosc. Relat. Phenom.* **16** 1
[23] Malterre D, Krill G, Durand J, Marchall G and Ravet M F 1986 *Phys. Rev.* B **34** 2176
       Haldane F D M 1977 *Phys. Rev.* B **15** 2477