Valence-level photoemission spectra of the actinide intermetallic compounds $ThPt_3$, UPt_5, UAu_3, and USn_3

W. -D. Schneider

Institut de Physique, Université de Neuchâtel, 2000 Neuchâtel, Switzerland

C. Laubschat

Institut für Atom- und Festkörperphysik, Freie Universität, 1000 Berlin 33, West Germany

B. Reihl

IBM Research Division, Zurich Research Laboratory, 8803 Rüschlikon, Switzerland

The valence-level excitations of the actinide intermetallic compounds $ThPt_3$, UPt_5, and UAu_3 have been investigated with resonant photoemission techniques, while those of USn_3 have been studied with x-ray photoemission. In all compounds, $5f$ spectral weight is found at the Fermi energy. Comparison of the spectra with calculated densities of states shows an overall agreement for the transition-metal d bands, but for UAu_3 reveals that the measured width of the $5f$ contribution is considerably larger than calculated. This behavior points to Coulomb correlation effects among the $5f$ electrons which may lead to excitation spectra reminiscent of those of Ce systems.

Some intermetallic compounds with a rare-earth or actinide atom as one of the constituents show exotic low-temperature properties like, e.g., enormous linear specific-heat coefficients. These materials have been called heavy-fermion systems[1] or heavy-electron metals,[2] since their effective electron masses must be orders of magnitude larger than the free-electron value. This behavior is believed to be closely related to the presence of the partially filled $4f$ or $5f$ shells.[3] Two different approaches to understanding the electronic structure of heavy-electron metals are presently being undertaken. The many-body theories start from the Anderson single-impurity model and then construct a lattice of such impurities to account for coherence effects.[4] In light rare-earth compounds, the single-impurity model has proven to be very successful for the description of ground-state properties and of high-energy spectroscopies.[5–7] In particular, the observed density of low-lying excitations in Ce metal is properly accounted for,[8] and this model can certainly be considered a correct first approximation of the electronic structure of Ce-based heavy-electron compounds like $CeCu_6$.[9] The single-impurity model has also been applied successfully to core-level spectra of various Th compounds where no direct overlap of the $5f$ wave functions is expected.[10,11] Recently, the first calculations for U impurities in metals within the Anderson model have been carried out and exhibit agreement with experiments on dilute alloys.[12]

The one-electron models start from first-principles band-structure calculations of the electronic structure in order to understand the normal-state high-temperature behavior of heavy-fermion systems. Since the interatomic distances between the rare-earth or actinide atoms are large in these compounds, the f wave functions do not overlap. Therefore, in these calculations special attention is devoted to the f-electron hybridization with ligand states.[13–15] In this way, a useful reference is obtained from which the low-temperature specific-heat enhancements, characteristic for many-body electron-electron correlations, can be estimated.[15] For Ce systems, this approach has been successful in determining ground-state properties like lattice constants and f occupation numbers,[16,17] but in correlated electronic systems the calculated eigenvalue distribution can never be compared directly to excitation spectra.[5] Sophisticated concepts had to be introduced into band calculations for the highly correlated and weakly hybridized $4f$ electrons in order to describe approximately the observed excitation spectra.[18,19] In the light actinide compounds, in general the $5f$ states are supposed to be strongly hybridized with ligand states.[15] For such systems, calculated densities of states (DOS's) seem to be better adapted for comparison with excitation spectra, since for extended states the eigenvalues can be identified with the ionization energies.[20] In fact, angle-resolved and resonant photoemission studies of UIr_3 showed good agreement with the calculated DOS, and the observed f-band dispersion followed closely that of the calculated energy bands.[21] Systematic calculations of the partial and total DOS's for the sequence UIr_3, UPt_3, and UAu_3 revealed important changes in the U $5f$ and transition-metal d hybridization.[15] Based on these computations, x-ray photoemission spectra (XPS) were recently calculated[22] and good agreement with experimental data[23] for UPt_3 and UAu_3 was found. On the other hand, spectroscopic evidence [photoemission and bremsstrahlung isochromat spectroscopy (BIS)] for Coulomb correlation effects among the $5f$ electrons has been reported for UPd_3,[24] UAl_2 and UPt_3,[25] and UNi_xCu_{5-x},[26] indicating the delicate balance of the $5f$ electrons between localization and itinerancy in U compounds.

The present paper presents and discusses valence-level spectra of ThPt$_3$, UPt$_5$, and UAu$_3$, excited with tunable synchroton radiation. The interest in these systems lies in the fact that ThPt$_3$ and UAu$_3$ may serve as reference compounds for the heavy-electron metal UPt$_3$.[23,10,15] The compound UPt$_5$, which shows no magnetic ordering down to 2.5 K,[23,27] does not seem to be far from heavy-electron behavior, since ligand substitution with Au (UPt$_4$Au) induces a heavy-fermion state.[28] The much better resolved spectra (0.25 eV) than those presented in an earlier work (1.2 eV),[23] and exploitation of the resonant enhancement of the 5f states,[29,30] provide detailed information for comparison with model calculations. In particular, the following items are discussed. (i) Identification of 5f symmetry in the valence-level excitations; (ii) differences between the width and shape of observed and calculated f contributions; (iii) overall shape of observed and calculated transition-metal DOS's; (iv) hybridization-induced split-off transition-metal d states in the energy region of the 5f states. Finally, as an example of a possible hybridization of 5f with ligand p states, a valence-level XPS spectrum of USn$_3$ is presented and interpreted in the context of band-structure calculations[31] for the isostructural compound UGe$_3$.

The polycrystalline samples were prepared and characterized as described in Ref. 23. The compounds UPt$_5$ and USn$_3$ crystallize in the cubic AuBe$_5$ and AuCu$_3$ structures, respectively. The interatomic U-U spacings are 5.25 and 4.6 Å. For ThPt$_3$ and UAu$_3$, the crystal structures are not known experimentally. The photoemission measurements of ThPt$_3$, UPt$_5$, and UAu$_3$ were performed in the photon-energy range $30 < h\nu < 130$ eV with a two-dimensional display-type spectrometer[32] at the Synchrotron Radiation Center of the University of Wisconsin-Madison. The XPS measurements of USn$_3$ were carried out in a Vacuum Generators ESCA-III spectrometer. To obtain clean surfaces, the samples were scraped *in situ* with a diamond file in a vacuum of better than 1×10^{-10} Torr.

Figures 1(a)—1(c) show valence-level photoelectron spectra of ThPt$_3$, UPt$_5$, and UAu$_3$ taken at 92-eV (dashed curves) and 98-eV (thick solid curves) photon energies, in order to take advantage of the resonant-intensity enhancement of the 5f-electron emission when the photon energy is swept through the 5d core-level threshold of the actinides.[29,30] While for uranium materials these photon energies correspond to the Fano minimum and maximum around the 5$d_{5/2}$ threshold, respectively, these energies also characterize the minimum and maximum of the conduction-band emission around the 5$d_{3/2}$ threshold for thorium materials.[30] Also shown in Fig. 1 are DOS calculations (thin solid curves) relevant for these compounds.[15] The limits of a pure atomiclike interpretation of the resonance phenomena in the presence of 5f-electron hybridization have been recently discussed.[33] For Ce systems, with their weakly hybridized 4f states, important progress in the interpretation of resonant photoemission data has been achieved.[34] Within the Anderson single-impurity model, the 4f contributions to the valence-level spectra at the 4d-4f resonance were calculated and found to be in fair agreement with the observed intensity distribution
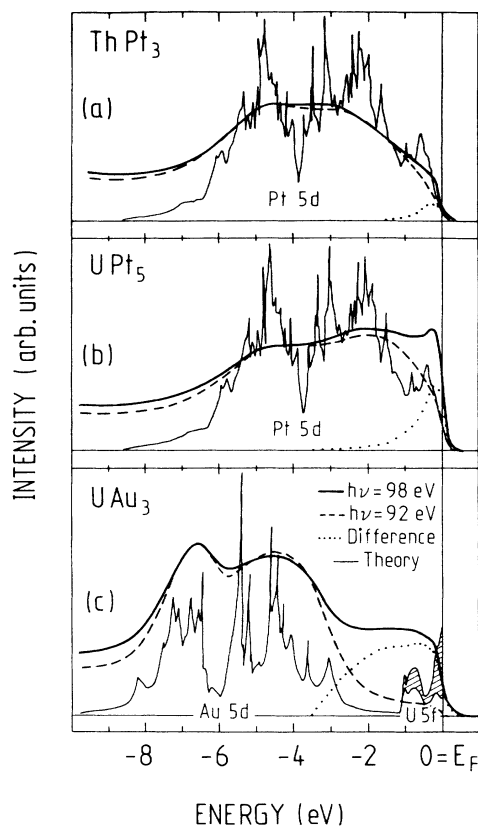

FIG. 1. Valence-level excitations of (a) ThPt$_3$, (b) UPt$_5$, (c) UAu$_3$ at resonance (thick solid curve) and off-resonance (dashed curve) to show the 5f spectral weight (dotted curve). The total instrumental resolution is 0.25 eV. For comparison (see text) the calculated (Ref. 15) DOS's are given as thin solid curves. The hatched area in (c) denotes the calculated partial f DOS.

and the photon-energy dependence. Based on this result, in first approximation it seems to be justified to interpret the difference between on-resonance and off-resonance spectra (dotted curve in Fig. 1) as the contribution of f symmetry states to the conduction bands. These curves were obtained by normalizing the two sets of spectra at the higher-lying maximum of the transition-metal d bands, since at these energies the contribution from 5f states appears to be negligible.[15] This rough subtraction procedure neglects the decrease in the d-emission cross section between 92 and 98 eV photon energy[35] and the increase in inelastic background owing to scattered 5f electrons.

Figure 1(a) displays the valence-level spectra of ThPt$_3$ recorded at the indicated photon energies which correspond to a minimum and near-maximum position in the partial electron yield[30,36] and electron-energy-loss curves[37] at the 5$d_{3/2}$-5f excitation threshold in Th systems. The on-resonance spectrum agrees well with an experimental XPS spectrum of ThPt$_3$ recorded with slightly poorer resolution.[10] Comparison with the off-resonance spectrum (dashed curve) reveals an enhanced emission intensity near E_F, indicating resonantly enhanced emission from

Th-derived $5f$ and $6d$ states.[36,38,39] The off-resonance spectrum reflects emission from states of different symmetries, where owing to the favorable cross-section ratio of $5d$ to other symmetries Pt $5d$ emission dominates. On comparison with a calculated[15] DOS of UPt_3, where the Fermi energy has been shifted by 0.5 eV towards higher binding energies to simulate $ThPt_3$ with its low $5f$ population, agreement between the gross features like bandwidth and position of the minimum between the spin-orbit split d bands is found. This correspondence between spectra and calculated DOS indicates that the one-electron model seems to be appropriate for the description of states with angular momentum $l < 3$.

Figure 1(b) shows the spectroscopic results for the valence levels of UPt_5. The overall shape of the Pt d emission is similar to the one of $ThPt_3$. In spite of the different crystal structures of the two compounds, this is not too surprising, since even for UPt_3 the band positions and gross features are not much different from those of the pure Pt metal.[15] To illustrate this point, the calculated DOS of UPt_3 is reproduced in Fig. 1(b). The difference between on- and off-resonance spectra (dotted curve) clearly reveals a considerable contribution of $5f$ spectral weight. Figure 2 shows a direct comparison between resonant photoemission data for UPt_3 (Ref. 40) and UPt_5 taken at the giant $5f$ resonance where the favorable $5f$-$5d$ cross-section ratio is exploited. Also, when the lower resolution of the UPt_3 data is accounted for, most of the $5f$ spectral weight in UPt_5 is distributed over a distinctly narrower energy range than in UPt_3. This can easily be seen by comparing the mean intensity ratio of the $5f$-derived peak near E_F and the Pt-derived $5d$ band, which remains constant in both spectra, although the U content in UPt_3 is nearly twice as large as in UPt_5. In an oversimplified rigid-band picture of the $5f$ states, this behavior could be understood as a lowering of the Fermi energy as observed[23] by the work-function increase in going from UPt_3 to UPt_5. Since the Fermi edge in UPt_3 falls into a small region of very high U $5f$ density,[15,25] lowering of the Fermi energy would not only lead to a charge transfer from U to Pt, but also to an immediate decrease of the $5f$

DOS at the Fermi level. Comparison of the calculated DOS of UIr_3, UPt_3, and UAu_3 (in the $AuCu_3$ structure) does indeed reveal such a lowering of the Fermi edge with respect to the $5f$ states between UPt_3 and UIr_3, while for UAu_3 a small rise is observed. On these grounds, one may speculate that substitution for a Pt by a Au atom in UPt_5 will cause a rise of E_F to a region of high $5f$ density as in the case of UPt_3. BIS spectra of UPt_3 and UPt_5 (Refs. 25 and 41) show a small decrease in width of the $5f$-derived structures near E_F, which points to another possible origin of the observed narrowing of the $5f$ emission in Fig. 2, namely, $5f$-band narrowing as a consequence of the higher U dilution in UPt_5. Both arguments are noncontradictory and detailed calculations are needed for UPt_5 to clarify the situation.

Figure 1(c) displays the valence-level excitations of the compound UAu_3. The on-resonance curve (thick solid curve) is consistent with previous XPS results of the same sample;[23] the off-resonance spectrum essentially reflects the transition-metal DOS in the compound. The most striking feature in the spectra is the broad and intensive distribution of $5f$ symmetry states (dotted curve) which differs clearly from those in UPt_3 and UPt_5. On the other hand, a similarly broad $5f$ spectral-weight distribution has also been observed for UPd_3 (Ref. 30) and for UCu_5.[42] Under the assumption that UAu_3 crystallizes in the cubic $AuCu_3$ structure, comparison with a recent band-structure calculation[15] for UAu_3 is shown as a thin solid curve in Fig. 1(c). The overall Au $5d$ features are well reproduced by the calculation. The hatched area near the Fermi edge represents the calculated partial f DOS.[15] It is evident from this figure that the measured width of the $5f$ contribution (dotted curve) exceeds considerably the calculated one. Since oxygen-induced $5f$ features can be excluded,[33] the obvious interpretation of this observation is that Coulomb correlations among the $5f$ electrons are present[25,43] which lead to a breakdown of the one-electron description of the $5f$ states. It appears that for some sufficiently diluted U intermetallic compounds, the $5f$ states should be better described by Anderson-type models, used so successfully for Ce compounds.

An important point of the band-structure calculations[14,15] is the prediction that hybridization between transition-metal d states and the f states removes states from the top of the transition-metal d band, and places them above the hybridization gap in the energy region of the $5f$ bands. In Fig. 1(c), these split-off d states are indicated by the lower line limiting the hatched area near E_F. In principle, these d states should show up in the off-resonance spectra but there is no clear indication of their presence. The ratio of the intensity maximum of the d emission (around 4 eV) to the intensity height around 1 eV binding energy is about 10, corresponding precisely to the ratio found in an XPS spectrum of pure Au.[44] Also, at 30 eV photon energy where the $5d$ to $5f$ cross section is large,[33,45] this ratio is still 9, which is not in favor of the presence of split-off d states in this energy region. Split-off states, however, are typical for materials crystallizing in the $AuCu_3$ structure.[46] Their absence in the UAu_3 spectra may well indicate that UAu_3 does not crystallize in this structure. It has been suggested to test the pres-
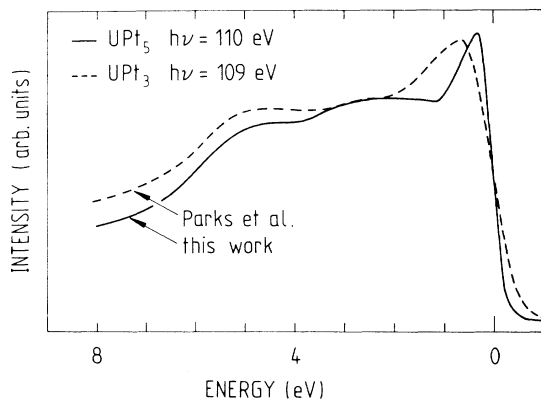

FIG. 2. Comparison between the valence-level excitations of UPt_3 (from Ref. 40) and UPt_5 (this work) recorded at the photon energies indicated.

ence of d symmetry around E_F using resonant $5p$-$5d$ excitation[14,15] which remains to be done in the future.

Finally, in Fig. 3 the XPS valence-level excitations (resolution 1.2 eV) of USn_3 are presented. In the sequence UPt_3-UAu_3-USn_3, the transition-metal d band moves towards higher binding energies so that in USn_3 the f-p hybridization will become dominant. The spectrum of this material, crystallizing in the cubic $AuCu_3$ structure and showing an enhanced linear specific-heat coefficient,[47,48] can be described in first approximation as a superposition of the valence-level spectra of α-U (Ref. 49) and Sn.[50] The prominent peak at E_F then arises predominantly from $5f$ states; the shoulder around 3 eV in accordance with the findings[51] for α-U, UGa_2, and UGa_3 from U $6d$ and to a lesser extent Sn $5p$ states, the hump at about 7 eV from the Sn $5s$ states. It is interesting to note that this spectrum of USn_3 is very similar to those obtained from the isostructural compounds UGe_3 and USi_3 where the $5f$ character of the peak at E_F has been established using different photon energies.[52] Since in USn_3 a direct $5f$-$5f$ overlap can be excluded (U-U spacing is 4.6 Å) it is concluded that a strong hybridization of the $5f$ states with conduction electrons occurs.[31] Band-structure calculations for the isostructural and isoelectronic (concerning the valence levels) compound UGe_3 predict $5f$-$4p$ hybridization caused by the participation of the $5f$ electrons in π bonding with the Ge $4p$ orbitals.[31] In analogy to this calculation, in Fig. 3 the dominant wave-function mixing is indicated in the corresponding spectral regions.

In closing, we want to emphasize that the low-temperature heavy-fermion properties like the enhancement of the linear specific-heat coefficient $\gamma(T\rightarrow0)$ are not directly connected to the density of states at the Fermi level. Rather, the enhancement reflects the strong f-electron correlation which manifests itself in the Anderson impurity model as the slope of the excitation spectrum at E_F, the scale of which is the inverse Kondo temperature: $\gamma(T\rightarrow0)$ proportional to $1/T_K$.[25] Consequent-
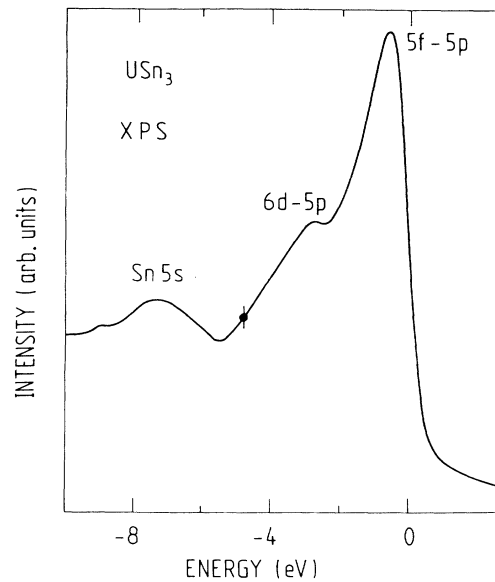

FIG. 3. XPS spectra of USn_3 excited with Al $K\alpha$ radiation ($h\nu=1486$ eV). The total instrumental resolution is 1.2 eV. The symmetry labels denoting the relevant wave-function mixing have been assigned to the peaks and the shoulder according to Refs. 31 and 50.

ly, these manifestations are expected to be observable in excitation spectra only at low temperatures and with an energy resolution of a few meV.

[1]G. R. Stewart, Rev. Mod. Phys. 56, 755 (1984).

[2]Z. Fisk, H. R. Ott, T. M. Rice, and J. L. Smith, Nature 320, 124 (1986).

[3]P. A. Lee, T. M. Rice, J. W. Serene, L. J. Sham, and J. W. Wilkins, Comments Cond. Matter Phys. 12, 99 (1986).

[4]N. d'Ambrumenil and P. Fulde, J. Magn. Magn. Mater. 47&48, 1 (1985), and references therein.

[5]O. Gunnarsson and K. Schönhammer, Phys. Rev. B 28, 4315 (1983).

[6]F. U. Hillebrecht, J. C. Fuggle, G. A. Sawatzky, M. Campagna, O. Gunnarsson, and K. Schönhammer, Phys. Rev. B 30, 1777 (1984), and references therein.

[7]W.-D. Schneider, B. Delley, E. Wuilloud, J.-M. Imer, and Y. Baer, Phys. Rev. B 32, 6819 (1985).

[8]F. Patthey, B. Delley, W.-D. Schneider, and Y. Baer, Phys. Rev. Lett. 55, 1518 (1985).

[9]F. Patthey, W.-D. Schneider, Y. Baer, and B. Delley, Phys. Rev. B 34, 2967 (1986).

[10]O. Gunnarsson, K. Schönhammer, D. D. Sarma, F. U. Hillebrecht, and M. Campagna, Phys. Rev. B 32, 5499 (1985).

[11]D. D. Sarma, F. U. Hillebrecht, O. Gunnarsson, and K. Schönhammer, Z. Phys. B 63, 305 (1986).

[12]A. C. Nunes, J. W. Rasul, and G. Gehring, J. Phys. C 19, 1017 (1986).

[13]D. D. Koelling, B. D. Dunlap, and G. W. Crabtree, Phys. Rev. B 31, 4966 (1985).

[14]R. C. Albers, Phys. Rev. B 32, 7646 (1985).

[15]R. C. Albers, A. M. Boring, and N. E. Christensen, Phys. Rev. B 33, 8116 (1986); R. C. Albers, A. M. Boring, P. Weinberger, and N. E. Christensen, ibid. 32, 7571 (1985).

[16]W. E. Pickett, A. J. Freeman, and D. D. Koelling, Phys. Rev. B 23, 1266 (1981).

[17]M. S. S. Brooks, J. Magn. Magn. Mater. 47&48, 260 (1985).

[18]M. R. Norman, D. D. Koelling, A. J. Freeman, H. J. F. Jansen, B. I. Min, T. Oguchi, and Ling Ye, Phys. Rev. Lett. 53, 1673 (1984).

[19]M. R. Norman, D. D. Koelling, and A. J. Freeman, Phys. Rev. B 31, 6251 (1985).

[20]T. Koopmans, Physica 1, 104 (1934).

[21]A. J. Arko, D. D. Koelling, and B. Reihl, Phys. Rev. B 27,

3955 (1983).

[22]P. Marksteiner, P. Weinberger, R. C. Albers, A. M. Boring, and G. Schadler, Phys. Rev. B **34**, 6730 (1986).

[23]W.-D. Schneider and C. Laubschat, Phys. Rev. B **23**, 997 (1981).

[24]Y. Baer, H. R. Ott, and K. Andres, Solid State Commun. **36**, 387 (1980).

[25]J. W. Allen, S.-J. Oh, L. E. Cox, W. P. Ellis, M. S. Wire, Z. Fisk, J. L. Smith, and A. J. Arko, Phys. Rev. Lett. **54**, 2635 (1985).

[26]F. U. Hillebrecht, D. D. Sarma, and N. Martensson, Phys. Rev. B **33**, 4376 (1986).

[27]P. H. Frings, Ph.D. thesis, University of Amsterdam, 1984.

[28]H. R. Ott, International Conference on Anomalous Rare Earth and Actinides, Grenoble, France, July, 1986 (unpublished); Annu. Rev. Mater. Sci. (to be published).

[29]R. Baptist, M. Belakhovsky, M. S. S. Brooks, R. Pinchaux, Y. Baer, and O. Vogt, Physica B **102**, 63 (1980).

[30]B. Reihl, N. Martensson, D. E. Eastman, A. J. Arko, and O. Vogt, Phys. Rev. B **26**, 1842 (1982).

[31]A. J. Arko and D. D. Koelling, Phys. Rev. B **17**, 3104 (1978).

[32]D. E. Eastman, J. J. Donelon, N. C. Hien, and F. J. Himpsel, Nucl. Instrum. Methods **172**, 327 (1980).

[33]Y. Baer, in *Handbook on the Physics and Chemistry of the Actinides*, edited by A. J. Freeman and G. H. Lander (North-Holland, Amsterdam, 1984), Vol. I, Chap. 4, p. 271.

[34]D. Gunnarsson and K. Schönhammer, in *Giant Resonances in Atoms, Molecules and Solids, NATO ASI Series B*, edited by J. P. Connerade, J.-M. Esteva, and R. Karnatak (Plenum, New York, 1987).

[35]J. Stöhr, G. Apai, P. S. Wehner, F. R. McFeely, R. S. Williams, and D. A. Shirley, Phys. Rev. B **14**, 5144 (1976).

[36]A. Fujimori and J. H. Weaver, Phys. Rev. B **31**, 6411 (1985).

[37]H. R. Moser, B. Delley, W.-D. Schneider, and Y. Baer, Phys. Rev. B **29**, 2947 (1984).

[38]D. Glötzel, J. Phys. F **8**, L163 (1978).

[39]H. L. Skriver and J.-P. Jan, Phys. Rev. B **21**, 1489 (1980).

[40]R. D. Parks, M. L. denBoer, S. Raaen, J. L. Smith, and G. P. Williams, Phys. Rev. B **30**, 1580 (1984).

[41]W. Grentz, C. Laubschat, and G. Kaindl (unpublished).

[42]W.-D. Schneider, B. Reihl, N. Martensson, and A. J. Arko, Phys. Rev. B **26**, 423 (1982).

[43]V. Zlatić, S. K. Ghatak, and K. H. Bennemann, Phys. Rev. Lett. **57**, 1263 (1986).

[44]G. K. Wertheim, J. Electron Spectrosc. Relat. Phenom. **6**, 239 (1975).

[45]S. M. Goldberg, C. S. Fadley, and S. Kono, J. Electron Spectrosc. Relat. Phenom. **21**, 285 (1981).

[46]C. Koenig, Z. Phys. B **50**, 33 (1983); F. U. Hillebrecht, J. C. Fuggle, G. A. Sawatzky, and R. Zeller, Phys. Rev. Lett. **51**, 1187 (1983); C. Laubschat, G. Kaindl, E. V. Sampathkumaran, and W.-D. Schneider, Solid State Commun. **49**, 339 (1984).

[47]M. R. Norman, S. D. Bader, and H. A. Kierstead, Phys. Rev. B **33**, 8035 (1986).

[48]M. H. van Maaren, H. J. van Daal, and K. H. J. Buschow, Solid State Commun. **14**, 145 (1974).

[49]Y. Baer and J. L. Lang, Phys. Rev. B **21**, 2060 (1980).

[50]R. A. Pollak, S. P. Kowalczyk, L. Ley, and D. A. Shirley, Phys. Rev. Lett. **29**, 274 (1972).

[51]B. Reihl, M. Domke, G. Kaindl, G. Kalkowski, C. Laubschat, F. Hulliger, and W.-D. Schneider, Phys. Rev. B **32**, 3530 (1985).

[52]D. P. Karim and D. J. Lam, *Abstract Booklet of Actinides '81 Conference* (Lawrence Berkley Laboratory, California, 1981).