Resonant photoemission study of $UNi_{5-x}Cu_x$

Wolf-Dieter Schneider

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

B. Reihl and N. Mårtensson

IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

A. J. Arko

Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439

Valence-band spectra of the intermetallic compounds $UNi_{5-x}Cu_x$ ($x=0.0$, 2.5, and 5) have been measured using synchrotron radiation in the energy range 10 to 130 eV. In all compounds the $5f$-derived valence-band density of states is pinned to the Fermi energy. In contrast to earlier work, no splitting of the U $5f$ emission due to different final-state $5f$ configurations is observed in UCu_5. This points towards an itinerant description of the $5f$ electrons in these compounds. A decrease in the intensity of the Ni two-hole satellite is observed in going from Ni metal and UNi_5 to $U(Ni_{0.5}Cu_{0.5})_5$ which can be related to a filling of the Ni d band. Furthermore, a shift of the Ni satellite energy by 1.3 eV towards higher binding energies occurs in $U(Ni_{0.5}Cu_{0.5})_5$.

INTRODUCTION

Intermetallic compounds of the actinides have stimulated considerable interest in the past due to their complex structural, magnetic, and superconducting properties. It is generally accepted that these properties are governed by the nature of the $5f$ electrons. Recently the existence of satellite structure in x-ray photoemission spectra (XPS) of several uranium compounds was shown to be due to the onset of a more localized behavior of the $5f$ electrons.[1] Also it has been realized, using resonant photoemission techniques, that the $6d$ electrons play an important role in determining the electronic and magnetic properties of $5f$ systems.[2,3] For the intermetallic compound system $UNi_{5-x}Cu_x$ with $x \geq 4$, van Daal et al.[4] proposed a possible mixed valence of uranium on the basis of lattice-constant, susceptibility, specific heat, electrical resistivity, and Seebeck coefficient measurements. This proposal of a mixed valence motivated Grohs et al.[5] to undertake an XPS study on these intermetallics. From valence-band and U $4f$ core-level spectra they concluded that UCu_5 is in a mixed-valent state (a mixture of U^{3+} and U^{4+}), whereas UNi_5 is assumed to have a pure U^{3+} state. However, the spectral features in the valence band of UCu_5, which were assigned to an initial $5f^2$ configuration, are weak, calling for a high-resolution study of the valence band of this interesting compound system. We have used tunable synchrotron radiation to examine the valence bands of UNi_5, $U(Ni_{0.5}Cu_{0.5})_5$, and UCu_5 to identify the U $5f$-derived features. Furthermore, we have applied resonant photoemission techniques[6] whereby the $5f$ character is first suppressed and then enhanced by tuning the photon energy through the binding energy of the U $5d$ core levels ($E_B \simeq 95$ eV). Additional insight into the electronic structure of $UNi_{5-x}Cu_x$, e.g., the d-band filling, is obtained by studying the two-hole satellites[7,8] in the constituents of these compounds.

EXPERIMENTAL

The photoemission measurements were performed with a display-type analyzer[9] using synchrotron radiation ($10 \leq h\nu \leq 130$ eV) at the Synchrotron Radiation Center of the University of Wisconsin-Madison. This system was operated in an angle-integrated mode with a full 86° acceptance cone of emission angles and with an energy resolution of ~ 0.15 eV. Typical peak intensities in the spectra are of the order of 10^5 counts per channel. Angle-integrated energy distribution curves (EDC's) were measured using a $\langle 100 \rangle$ oriented single crystal of UNi_5 and polycrystalline samples of $UNi_{5-x}Cu_x$ ($x=2.5$ and 5). The $UNi_5(100)$ surface was prepared by Ne-ion etching and anneal-

ing. Its surface conditions were monitored using Auger spectroscopy and low-energy electron diffraction (LEED). The polycrystalline samples were filed with a diamond file and studied *in situ* in a vacuum of better than 1×10^{-10} Torr. The UCu$_5$ sample—crucial for the question of mixed valence—was measured as-cast[4] and well annealed yielding essentially the same photoemission spectra.

RESULTS AND DISCUSSION

In Fig. 1, EDC's are shown for UNi$_5$ for $30 \leq h\nu \leq 80$ eV. The intensity of structure A follows the well-known energy dependence of the $5f$ cross section[10] and is therefore identified with $5f$-electron emission. This feature A shows no shift in binding energy in going through the compound series, a fact which confirms recent XPS measurements on intermetallic U-Pt and U-Au systems.[11] A clear view of the $5f$-derived features is possible when spectra taken below the onset of the $5d$-$5f$ resonance (92 eV) are compared with spectra at resonance[6] (98 eV), as shown in Fig. 2. The $5f$ contribution which emerges at resonance is not visible at $h\nu = 92$ eV. In order to extract information on possible changes of the $5f$ occupation in these compounds, difference spectra (also shown in Fig. 2), were generated in the following way: The spectra taken at 92- and 98-eV photon energy were normalized at 2.5 and 4 eV since the d-band
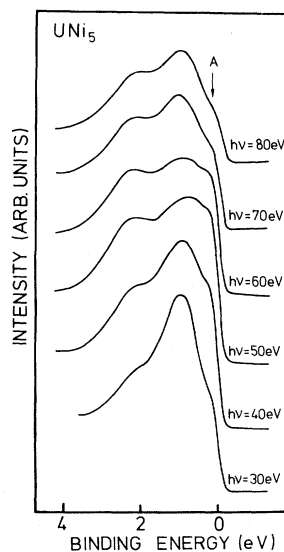

FIG. 2. EDC's for UNi$_5$, U(Ni$_{0.5}$Cu$_{0.5}$)$_5$, and UCu$_5$ at resonance ($h\nu = 98$ eV) and off-resonance ($h\nu = 92$ eV) to show the $5f$-related emission features. The spectra are normalized at 2.5 and 4 eV.

features at higher binding energies are considered to be less affected by $5f$-electron contributions. With this normalization the $5f$-derived intensity in UCu$_5$ is overestimated by about 18% when compared with the one in UNi$_5$, since this is the photoionization cross-section difference between the Ni and Cu $3d$ bands.[12] (The difference in the photoionization cross section between 92- and 98-eV excitation energy is only about 5% for the Ni and Cu $3d$ bands, respectively.) Consequently, the resulting difference spectra were integrated from 2.2-eV binding energy up to the Fermi energy and then corrected by the $3d$ cross-section variation between Cu and Ni. Then the intensities of the $5f$ contribution to the spectra do not change by more than 10% in all compounds. This leads immediately to the conclusion that the number of f electrons does not change substantially in these compounds.

We do not observe any $5f$ satellite structure in the valence bands at the U $5d$-$5f$ resonance, as has recently been found in α-U.[13] From these observations (no different $5f$ multiplets in the $5f$ valence bands, no satellites) we conclude that there is no hint of an increased $5f$ localization, i.e., this compound system may not simply be related to a

FIG. 1. EDC's for UNi$_5$ at various photon energies. Peak A indicates the photon-energy-dependent $5f$ emission.

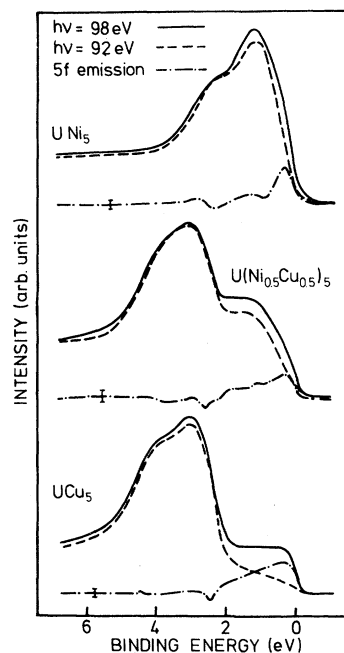mixed-valent situation with different final-state multiplets in the photoemission spectra as encountered in rare-earth compounds.[14] In fact, the pinning of the $5f$ emission at E_F (cf. Fig. 2) points towards an itinerant description of the f electrons in these compounds, even though the U-U distance (UNi$_5$: 4.796 Å) is bigger than in clearly localized U compounds,[1-3] which indicates that hybridization effects with Ni and/or Cu $3d$ electrons are important. These findings are contradictory to those reported by Grohs et al.[5] A possible reason for this discrepancy between our valence-band spectra of UCu$_5$ and the one taken by Grohs et al.[5] may lie in the sensitivity of this compound to oxidation. After oxygen exposure we observed in UCu$_5$ a shoulder on the leading edge of the Cu $3d$ band at 1.5-eV binding energy indicating an initial-state $5f^2$ configuration due to UO$_2$ formation. Figure 3 shows exemplary data for this effect.

Now we discuss the overall appearance of the density of states in this compound system. The remaining structures in Figs. 1 and 2 are easily identified with the Ni and Cu d bands, respectively. The shape and the relative positions correspond well with the existing literature for Ni-Cu alloys, e.g., Ref. 15. In comparing the off-resonance spectra ($h\nu=92$ eV) for the ternary compound with the pure Ni spectrum of Ref. 7 one clearly recognizes a shift of the band maximum to higher binding energies indicating d-band filling on alloying. A similar d-band filling in uranium compounds has previously been reported for the U-Pt system.[11]

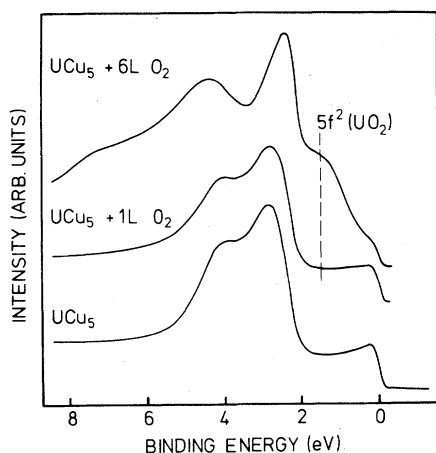

FIG. 4. EDC's for UNi$_{5-x}$Cu$_x$, taken at their respective Ni $3p\leftrightarrow3d$ ($h\nu=67$ eV) and Cu $3p\leftrightarrow3d$ ($h\nu=76$ eV) two-hole satellite resonance maxima. The spectra were normalized to equal valence-band emission down to 6 eV below E_F.

Further information on the Ni d-band filling is obtained by using resonant photoemission techniques at the Ni $3p$-$3d$ resonance corresponding to a photon energy of ~67 eV. Here a $3p$ electron is excited to the $3d$ valence band and followed by a super-Coster-Kronig decay ($3p^53d^{n+1}$ $\rightarrow3p^63d^{n-1}\epsilon f$). This ionization channel interferes with the direct excitation of the $3d$ valence band leading to Fano resonances and to a two-hole bound satellite in photemission.[16] Owing to this coupling of the $3p\rightarrow3d$ absorption, the intensity of the two-hole satellite at resonance is sensitive to any change in the occupation of the Ni $3d$ band.

Figure 4 summarizes our results on valence-band satellites in the compounds. We find a two-hole satellite in UNi$_5$ and a weak one in U(Ni$_{0.5}$Cu$_{0.5}$)$_5$. The relative intensity of this satellite as compared to the main $3d$ emission is about the same in Ni and UNi$_5$ ($\sim23\%$) (the value for pure Ni is estimated from the data of Refs. 7 and 17) and $\sim5\%$ in U(Ni$_{0.5}$Cu$_{0.5}$)$_5$. The weakness of this satellite in the ternary compound indicates a close relationship of the satellite intensity with the number of available holes in the Ni d band.[18,19] On the other hand, the resonance satellite in Cu shows no

FIG. 3. EDC's for UCu$_5$ at $h\nu=50$ eV. The influence of oxide contamination at the leading edge of the Cu $3d$ band is indicated by the dashed line.
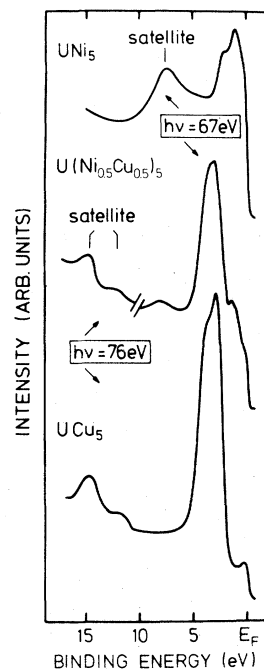
change in intensity and in binding energy (11.8 and 14.8 eV) in going from Cu metal[8] to UCu_5 and $U(Ni_{0.5}Cu_{0.5})_5$ (see Fig. 4).

The relative energy of the Ni satellite with respect to the main $3d$ emissions increases from 6 eV in Ni metal to 6.3 eV (7.45 eV) in UNi_5 and 7.3 eV (8.2 eV) in the more dilute $U(Ni_{0.5}Cu_{0.5})_5$ compound. The numbers in parentheses are the absolute energy values. This trend is understandable in terms of $3d$-band filling: a lowering of the Ni d band with respect to the Fermi energy means increased confinement of the Ni d shell and therefore increased localization of the $3d$ electrons at the Ni site. However, for a detailed treatment of the satellite position one has to consider how the double-hole screening charge (the final-state charge distribution resembles that of a Zn impurity atom) interacts with the surrounding lattice.

The decrease of the Ni-satellite intensity in $U(Ni_{0.5}Cu_{0.5})_5$ emphasizes its resonant origin: with a decreasing number of d holes the probability for transitions to unoccupied orbitals decreases in the final state. On the other hand, a full Ni d band should lead to a Cu-type satellite in the spectrum, an excitation which involves the singular response of the $4s$-$4p$ bands leading to the same d^8 configu-

ration in the final state.[16] Even if there were, in the case of $U(Ni_{0.5}Cu_{0.5})_5$, a finite $3d$-$4s$ hybridization which would lead to partly empty d states and which would favor direct $3p \rightarrow 3d$ transitions, this contribution to the resonance enhancement of the satellite will be relatively small.

To summarize, high-resolution resonance experiments with synchrotron radiation show no evidence for two different final-state $5f$ multiplets in the valence bands of UCu_5, indicating itinerant $5f$-electron behavior partly due to hybridization with $3d$ electrons. The Ni $3d$-band filling in these compounds is accompanied by a shift of the Ni band maximum to higher binding energies. It also manifests itself through the decrease of the intensity of the two-hole satellite.

ACKNOWLEDGMENTS

[1]W. D. Schneider and C. Laubschat, Phys. Rev. Lett. 46, 1023 (1981).

[2]B. Reihl, N. Mårtensson, P. Heimann, D. E. Eastman, and O. Vogt, Phys. Rev. Lett. 46, 1480 (1981).

[3]B. Reihl, N. Mårtensson, D. E. Eastman, and O. Vogt, Phys. Rev. B 24, 406 (1981).

[4]H. J. van Daal, K. H. J. Buschow, P. B. von Aken, and M. H. van Maaren, Phys. Rev. Lett. 34, 1457 (1975).

[5]H. Grohs, H. Höchst, P. Steiner, S. Hüfner, and K. H. J. Buschow, Solid State Commun. 33, 573 (1980).

[6]R. Baptist, M. Belakhovsky, M. S. S. Brooks, R. Pinchaux, Y. Baer, and O. Vogt, Physica (Utrecht) B102, 63 (1980).

[7]C. Guillot, Y. Ballu, J. Pagné, J. Lecante, K. P. Jain, P. Thiry, R. Pinchaux, Y. Pétroff, and L. M. Falicov, Phys. Rev. Lett. 39, 1632 (1977).

[8]M. Iwan, F. J. Himpsel, and D. E. Eastman, Phys. Rev. Lett. 43, 1829 (1979).

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

[10]D. E. Eastman and M. Kuznietz, Phys. Rev. Lett. 26, 846 (1971).

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

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

[13]M. Iwan, E. E. Koch, and F. J. Himpsel, Phys. Rev. B 24, 613 (1981).

[14]M. Campagna, G. K. Wertheim, and E. Bucher, Struct. Bonding (Berlin) 30, 99 (1976).

[15]K. Y. Yu, C. R. Helms, W. E. Spicer, and P. W. Chye, Phys. Rev. B 15, 1629 (1977).

[16]L. C. Davis and L. A. Feldkamp, Phys. Rev. B 23, 6239 (1981).

[17]F. J. Himpsel, P. Heimann, and D. E. Eastman, J. Appl. Phys. 52, 1658 (1981).

[18]M. R. Thuler, R. L. Benbow, and Z. Hurych (unpublished).

[19]J. C. Fuggle and Z. Zolnierek, Solid State Commun. 38, 799 (1981).