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High resolution photoemission on UPdSn and UNiAl

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Abstract

High-resolution UV photoelectron spectroscopy on heavy-fermion antiferromagnet UNiAl displays a broad triangular 5f emission spread from E_F down to at least -1 eV. The presence of 5f states at E_F , in contrast to the low γ value of $5 \text{ mJ mol}^{-1} \text{ K}^{-2}$, is observed also in local-moment antiferromagnet UPdSn. The considerable degree of itinerancy is demonstrated in both cases by 4f core-level spectra.

1. Introduction

Variations in the 5f electron localization of actinide intermetallics can lead to different types of ground state. Photoelectron spectroscopy is in principle a powerful method for following details of the localization process on a microscopic scale. However, it is not yet clear the extent to which the photoemission spectra are affected by final-state effects in the case of materials with strong electron–electron correlations, or the extent to which they reflect the underlying single-particle electronic structure. The aim of the present investigation is to contribute to the understanding of the basic characteristics of the electronic structure of uranium intermetallics. We have concentrated on photoemission spectroscopy studies on ternary uranium compounds of the type UTX. Systematic research of their bulk properties has provided a good background for studies using microscopic methods. Variation in the T and X components provides a wide spectrum of physical behaviour. For an introductory study, two of them, UNiAl and UPdSn, were selected as representatives of different classes of compounds. UNiAl is antiferromagnetic below $T_N = 19$ K, but the slow magnetic saturation in fields above the metamagnetic transition ($B_c = 11.3$ T) and the low magnetic moments (about $0.6 \mu_B$ per uranium atom) indicate an itinerant character of the magnetism. Also the high γ value of $164 \text{ mJ mol}^{-1} \text{ K}^{-2}$ indicates the presence of itinerant

5f states at E_F [1]. On the contrary, the γ coefficient of UPdSn is only about $5 \text{ mJ mol}^{-1} \text{ K}^{-2}$ [2–4]. This value is extraordinarily low among uranium intermetallics and can, together with the considerable size of the ordered magnetic moments on the U atoms ($2.1 \mu_B$ per uranium atom [5]), be explained as a consequence of localization of the 5f states. The reason for the existence of localized 5f states in UPdSn (or at least more localized than in UNiAl) can be the different geometrical arrangement of the uranium atoms (only two nearest neighbours at a distance of 365 pm) and/or a reduced 5f–d hybridization. Inspecting possible analogies in the broad spectrum of uranium intermetallic compounds, we can find only one compound with such a low γ value, namely UPd₃, where the shift of 5f states from E_F is documented by electron spectroscopy [6–8].

2. Experimental details and discussion

Polycrystalline samples of UNiAl and UPdSn were prepared by arc melting of stoichiometric amounts of the constituents. The surface was cleaned by sputtering by Ar^+ ions during heating to 150 °C. The spectra were recorded at $T=77 \text{ K}$. A stoichiometric surface was obtained by *in-situ* scraping using a diamond file. The variation in the composition upon different preparation procedures was monitored by the evaluation of the integral intensities of the core level lines. The compositions of the surfaces subjected to standard Ar^+ ion sputtering (argon at $8 \times 10^{-5} \text{ Torr}$; 3 keV), which is used below for comparison with the stoichiometric surface, correspond to $\text{U}_{1.45}\text{Pd}_{1.12}\text{Sn}_{0.43}$ and $\text{U}_{1.2}\text{NiAl}_{0.8}$. The O 2p features were negligible in all spectra for at least 30 min, which demonstrates the good quality of the surface.

Valence band spectra of UPdSn were recorded for the excitation energies $h\nu=16.8 \text{ eV}$ (Ar I), 21.2 eV (He I) and 40.8 eV (He II). The instrumental resolution combined with the Fermi level temperature broadening at 77 K corresponds to a resolution Δ ranging from 50 to 100 meV depending on the electron analyser pass energy E_0 . Spectra obtained by X-ray photoelectron spectroscopy (XPS) with Al K α excitation ($h\nu=1486.6 \text{ eV}$) display $\Delta \approx 0.8 \text{ eV}$. The absolute accuracy of the calibration of the energy analyser voltage, which was checked by the position of the gold Fermi edge, is better than 5 meV in UV photoelectron spectroscopy (UPS) and better than 100 meV in XPS.

All experimental spectra were refined in a standard way by applying a correction for the transmission function of the energy analyser, and subtracting the secondary-electron background. In the case of Ne I spectra, the doublet ($h\nu=16.67$ and 16.85 eV) was first separated. We are aware of the fact that the secondary-electron background subtraction procedures are most reliable for higher kinetic energies (XPS, He II), while some arbitrary estimates are necessary to cope with the strong background variation and its high intensity for low kinetic energies of photoelectrons, which is crucial for Ne I and He I spectra.

Valence band spectra for different excitation energies obtained on a scraped surface are displayed in Figs. 1 and 2 for UNiAl and UPdSn respectively. The basic features are compatible with what was found earlier for palladium and nickel intermetallics in general [9]. In a compound with the more electropositive uranium, the spectral intensity coming from Ni(Pd) d states is shifted from E_F to higher binding energies leaving conduction electron states of uranium near E_F . Thus the maxima found at around -2 eV for UNiAl and at around -3.5 eV for UPdSn can be mainly attributed to 3d and 4d emission respectively. This assignment is directly supported by results on ThPdAl and LaPdAl [9], where the XPS spectra were found to be dominated by a single pronounced maximum at around -4 eV. A more quantitative analysis based on atomic photoionization cross-section calculations [10] shows that the cross-section of the 5f emission should increase relatively to the Ni 3d emission with increasing photoexcitation energy. Thus the development of the UNiAl spectra from $h\nu=21.2$ eV to $h\nu=40.8$ eV shows that the spectral intensity, which is spread from E_F towards the minimum, should be attributed mainly to the emission of 5f origin. A standard procedure of separation of the 5f emission is to subtract the spectra taken at $h\nu=21.2$ and 40.8 eV, normalized at higher binding energies, where the 5f emission is no longer expected. The result, which is severely affected by details of the background subtraction and normalization procedures, must be used with caution. Moreover, electron structure calculations (*e.g.* for UCoAl [11]) show

Fig. 1. Valence-band photoemission spectra of UNiAl (stoichiometric surface) recorded for different excitation energies. The shaded area is an estimate of the 5f emission obtained by the procedure described in text.

Fig. 2. Valence band photoemission spectra of UPdSn (stoichiometric surface) recorded for different excitation energies. The shaded area is an estimate of the 5f emission obtained by the procedure described in text.

that the 5f-d hybridization causes some portion of the d partial density of states (DOS) to appear (or to be induced) at the maximum of the 5f DOS and vice versa. Similar mechanisms (hybridization of d and 5f states with s, p and 6d states forming a broad conduction band) can be responsible for the shape of the spectra obtained at $h\nu=16.8$ eV, which mimic the features found for higher excitation energies even if the 3d and especially the 5f cross-sections are very small for such low excitation energies.

The relatively broad triangular 5f emission, observed for UNiAl in the case of He II radiation, is a rather conventional picture for most of the uranium intermetallics including heavy-fermion compounds [12]. A comparison with the spectra obtained on a sputtered (uranium-rich) surface shows that some additional 5f intensity appears for the stoichiometric surface in the energy range below -0.3 eV. Although the influence of nickel-related states (3d) cannot be excluded, one would expect a stronger effect in the He I spectrum in the case. Assuming a 5f origin of this feeble feature, we still cannot decide whether it is an unresolved satellite superimposed on the single-particle DOS, which is suppressed for the sputtered surface, or a feature of the 5f band. The excess of uranium in the sputtered surface causes a reduction in the mean U-U spacing and possible subsequent delocalization and loss of correlation features. Such a satellite can originate possibly from poorly screened 5f final states [12].

In UPdSn, the larger separation of the 4d states from E_F causes their energy overlap with electronic states around E_F to be reduced. Photoionization cross-section calculations [10] show here that the spectra should be dominated by the Pd 4d emission, which is considerable already for $h\nu=16.8$ eV, and only some admixture of the 5f emission can be expected at higher excitation energies. This makes the separation of the 5f emission even more uncertain than in UNiAl, but the increase in the emission at E_F with increasing excitation energy indicates again the 5f character of the states close to E_F , which is in contradiction with the low γ value. The noticeable shoulder centred at around -0.6 eV is quite similar to the localization features ($5f^{n-1}$ final state) observed in UPd₂Si₂ [8]. This approach, however, fails to explain why this shoulder becomes relatively more pronounced when the excitation energy is decreased even down to $h\nu=16.8$ eV, where almost no 5f emission is possible. Such a development could suggest a Pd 4d or U 6d origin of this shoulder. Comparison with the uranium-rich surface shows that the reduction in the uranium content depresses strongly the emission at E_F , but the satellite becomes relatively enhanced. Thus Pd 4d states are the most plausible source of major part of spectral intensity in this shoulder.

The U 4f core level spectra obtained on both compounds are displayed in Fig. 3. For UNiAl, they are of the type found for uranium compounds with a broad 5f band, *i.e.* both the position and the shape of the 4f spectral lines resemble those of α -U [13]. As comparison of the data obtained on the scraped and the sputtered surface shows, the full width at half-maximum is slightly higher in the stoichiometric case (2.5 eV in contrast with 2.2–2.3 eV in the uranium-rich case). Although no satellite structure can be observed,

Fig. 3. U 4f core level spectra (spin-orbit split $4f^{6/2}$ and $4f^{7/2}$ doublet) obtained on stoichiometric (scr.) and uranium-rich (sp.) surfaces of UNiAl and UPdSn.

the spectrum can be decomposed into two asymmetric gaussians and broad features located at around -6 eV with respect to the main lines. In UPdSn, the main 4f spectral lines are somewhat shifted to higher binding energies (by about 0.4 eV) with respect to UNiAl and UPdSn subjected to sputtering, but still the position of these main lines shows well-screened final states, *i.e.* a high probability of screening by 5f electrons. This implies that some itinerant character of the 5f states must be retained. The main lines are, however, accompanied by a pair of satellites at higher binding energies, separated from the main lines by 2.6 eV and 6.4 eV respectively. This spectrum is similar to what has been found for example for UCu_5 . Sarma *et al.* [14] analysed such a type of spectrum using the Gunnarsson-Schönhammer model and concluded that the 5f states can be only weakly hybridized but that the correlation energies are considerable.

3. Conclusions

High resolution UPS and XPS shows for UNiAl the 5f emission to be spread down to about -1 eV from E_F . The correlation features are weaker than expected for a compound exhibiting magnetic ordering. The situation in UPdSn is much less clear. Part of the spectral intensity, which can be attributed to the Pd 4d states, forms a shoulder at around -0.6 eV. The presence of these states in the vicinity of E_F can point to the 5f-4d hybridization, which implies an itinerant character of 5f states. A considerable spectral intensity, probably of the 5f origin, was found at E_F , which is in contrast with the low γ value. However, the energy resolution of the spectroscopy is too poor to visualize details of those states at around E_F , which are thermally accessible in the low temperature region, from which the low γ is extracted. In particular the 4f core level spectra show that a considerable itinerancy of the 5f states is retained in this compound.

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