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Correlation between ligand density of states and 5*f* delocalization in uranium intermetallic compounds

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We report spectra of the unoccupied states of uranium intermetallic compounds which contain both localized and delocalized final states. The intensity of the delocalized final states scales with the density of ligand states in the region of the occupied 5*f* state. The density of ligand states is an important factor influencing the detailed nature of the 5*f* states in U intermetallic compounds.

The electronic structure of intermetallic U compounds, especially those exhibiting heavy-fermion behavior at low temperatures, is presently receiving a lot of attention. As a starting point for the characterization of U compounds, one often uses the so-called Hill plot.[1] In this picture a correlation is suggested between the U-U distance and the degree of localization of the 5*f* states: If it is larger than 3.4–3.6 Å, the 5*f* states are expected to be localized. If the U-U distance is smaller than this critical value, a 5*f* band is formed. Spectroscopic investigations, however, indicated that this simple correlation may be incorrect. For example, the 5*f* states of UIr_3 should be localized, as the U-U separation is 4.023 Å. In contrast to this prediction, *f*-band dispersion was observed by angle-resolved photoemission from a single crystal.[2] An alternative starting point is to look for other metals, which by virtue of a similar electronic ground-state configuration may be expected to show similar behavior. Ce is such a metal. Various models have been proposed to explain photoemission of Ce compounds. In all these models hybridization between Ce 4*f* and transition-metal *d* states is an important factor influencing the 4*f* spectral function,[3,4] despite the fact that the radial extension of the 4*f* wave function is smaller than that of the outer valence orbitals.[5] The influence of *f*-*d* hybridization should be much stronger for U compounds, since the 5*f* wave function is sufficiently extended to form a 5*f* band in U metal. In contrast to that, the 4*f* states in Ce metal are highly localized. Therefore, comparing Ce and U, we expect to find a similar, or even more pronounced influence of ligands on the U 5*f* level than has been observed for the Ce 4*f* level in Ce compounds. As an example we consider the quasibinary series UNi_xCu_{5-x}. "Low-energy" measurements (susceptibility, lattice constant, specific heat) have been interpreted in terms of a fully localized nonmagnetic $5f^2$ ground state for UNi_5, and a fluctuation between $5f^2$ and $5f^3$ configurations for Cu-rich alloys.[6] X-ray photoemission spectroscopy (XPS) measurements, however, did not confirm the proposed localized $5f^2$ initial-state configuration for UNi_5.[7] Resonant photoemission for these and other compounds pointed towards the importance of hybridization or even delocalized 5*f* states.[2,8,9] In this Communication we report spectra of the unoccupied electronic states of these compounds, obtained by bremsstrahlung isochromat spectroscopy (BIS). The 5*f* states contain two different features which are interpreted as localized and delocalized final states. It is found that the density of ligand states is an important factor influencing the detailed nature of the 5*f* states in U compounds.

The samples were prepared by melting in an induction-heated levitation crucible, and characterized by metallography and x-ray diffraction. An upper limit for oxide concentration due to oxygen uptake during the reaction is 10^{-4}. The samples were cleaned *in situ* by scraping with a ceramic file. Contamination was controlled by monitoring the O 1*s* and C 1*s* lines. The 4*f* core level, as well as the valence-band spectra recorded by x-ray photoemission are in close agreement with published data.[7] Bremsstrahlung isochromat measurements yielding spectra of the unoccupied states were performed with a cylindrical Pierce-type electron gun using a large-solid-angle monochromator to define the x-ray window. The resolution was 0.8 eV for BIS and 0.7 eV for XPS.

In Fig. 1 the occupied[7] and unoccupied valence states of UNi_xCu_{5-x} and $ThNi_5$ are shown. Below E_F, the spectra are, to a large extent, dominated by the Ni or Cu *d* states. Closer inspection shows that the UNi_5 valence band is somewhat rounded due to the presence of the 5*f* electrons. For UCu_5 the 5*f* states can be seen close to E_F, superimposed on the Cu *s* states. The BIS spectra of the U compounds exhibit a pronounced structure near E_F, which extends up to 5–7 eV above E_F. The BIS spectrum of $ThNi_5$ demonstrates that the empty Ni *d* states do not give rise to a structure comparable in intensity to the 5*f* states which for $ThNi_5$ are at 4.7 eV above E_F. Also, we can see that the actinide 6*d* and 7*s* states only cause a flat and featureless background onto which the 5*f* structures are superimposed. Consequently, the structures between E_F and 5–7 eV above which are found in the BIS spectra of the U compounds can be identified with U 5*f* final states. The shape of the 5*f* part changes with the ratio of the concentration of Ni to Cu, and is always very different from the 5*f* peak found for $ThNi_5$. For the U compounds, we find that the kink marking the upper edge of the 5*f*-derived emission moves to higher energy with increasing Ni content. However, the 5*f* structure does not keep its shape while shifting to higher energy. In UCu_5, the peak of the 5*f* structure is at about 1.2 eV above E_F, and although the 5*f* upper edge moves to higher energy with increasing Ni content, the peak stays at that position and gains intensity, whereas the part which is shifting upwards decreases in intensity. These changes lead

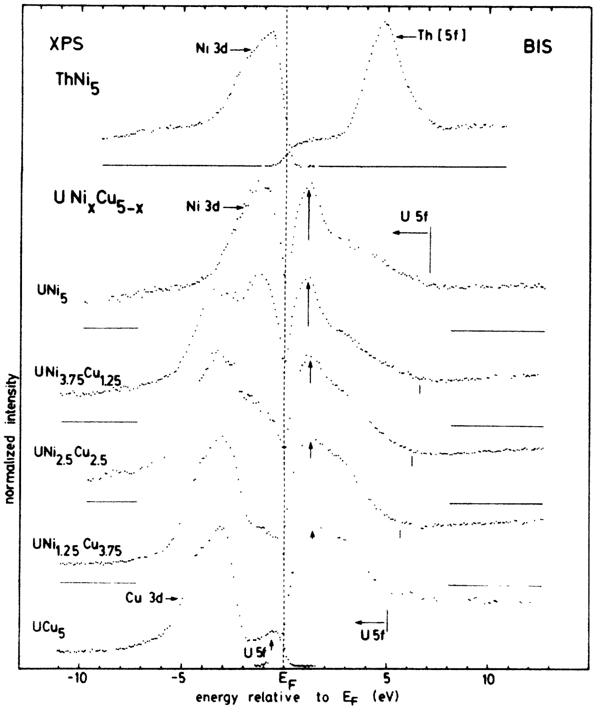

FIG. 1. Occupied and unoccupied valence states for $ThNi_5$ and UNi_xCu_{5-x} compounds. All spectra have been normalized to constant peak height. In $ThNi_5$, the $5f$ states form a band centered at 4.7 eV above E_F. In the BIS spectra of U compounds, the $5f$ signal is between E_F and 5–7 eV above E_F; upper edge is indicated by tick marks. Arrows in BIS spectra indicate the delocalized final state.

to a pronounced peak at 1.2 eV above E_F for UNi_5. As we have discussed above, the contribution of Ni *d* states is negligible compared to that of the $5f$ states. Also, this spectrum cannot be explained by bandlike $5f$ states within a single-particle picture, because then it should be similar to that of $ThNi_5$, only with the $5f$ peak shifted in energy. A $5f^4$ localized configuration in the final state does not account for the observed spectrum, since then we expect a total width of roughly 4 eV,[10] as opposed to 5–7 eV found in the experiment. Furthermore, the shape and the changes of shape cannot be understood in terms of a localized f^4 final state alone. Neither of the final states, bandlike or localized, by itself can explain the experimental result. Consequently, we propose that the BIS spectrum of UNi_5 is composed of *both* these transitions, which lead to quite different final states. One of them can be described as a $5f^3$–$5f^4$ transition, yielding the intensity at higher energy. The shape and width of this contribution is determined by multiplet splitting. Due to lifetime broadening and/or lack of resolution, this splitting cannot be resolved. For the peak close to E_F we know that it must also be due to $5f$ states. The position of this peak close to E_F suggests that it is due to a delocalized final state, i.e., the $5f$ occupancy on the site where the transition takes place, does not change. In other words, in this transition a $5f$ electron has been added which has a high probability to hop to other sites. Such a transition is possible if the hybridization between the $5f$ level and the extended states is large.

The sequence of spectra in Fig. 1 shows that there is a continuous increase of the delocalized part with increasing Ni content. The occupied states show a marked increase of the *d*-like density of states in the region of the occupied $5f$ levels as Ni is added. These two findings complement each other. The $5f$ states will be more affected by hybridization if there are more extended states in the energy region of the occupied $5f$ levels. This is clearly the case for increasing Ni content. We can conclude that the density of states is a very important factor influencing the detailed nature of the $5f$ states.

The results presented here are in some respects similar to what was found for nonmagnetic Ce compounds.[11-13] BIS spectra of such compounds also exhibited a localized ($4f^2$) and delocalized ("$4f^1$") final state. The delocalized final state was interpreted within an Anderson impurity model[14] as being associated with the Kondo singlet ground state which does not show a localized magnetic moment. Nonmagnetic U compounds like UNi_5, UPt_4Ir,[15] and UIr_3 (Ref. 16) show BIS spectra similar to those of nonmagnetic Ce compounds, and one might propose to use the same model to understand U compounds. However, if the *f*-*f* interaction was found not to be important for Ce compounds, the situation may be different for U compounds. Results for U-Si, as well as for U-Pt compounds,[16] show an increase of the delocalized part as the U-U distance is reduced and the overlap between $5f$ wave functions increases.

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