Appearance of Correlation Effects in U Intermetallics

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Experimental densities of states of USi_3 and UIr_3 obtained by x-ray photoelectron spectroscopy and bremsstrahlung isochromat spectroscopy (BIS) are compared to fully relativistic self-consistent band-structure calculations. Very good agreement is found for USi_3, whereas the unoccupied states of UIr_3 exhibit a satellite which cannot be explained by the one-particle calculation. The satellite in BIS of UIr_3 is attributed to a quasiparticle bound state, and is qualitatively reproduced by a Hubbard model including Coulomb correlation within the narrow $5f$ band. The importance of our findings with reference to the magnetic properties of U intermetallics as well as pure U metal is discussed.

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Open-shell f electrons in the lanthanides and actinides give rise to many interesting physical properties and have generated lively discussion concerning itinerant versus localized character.[1] This is primarily due to a strong interplay between Coulomb correlation among the f-level electrons and their hybridization with band states. The anomalous behavior of the Ce- and U-based heavy-fermion superconductors has given further impetus to the study of f-electron systems. X-ray photoelectron spectroscopy (XPS) and bremsstrahlung isochromat spectroscopy (BIS) offer the possibility to study directly the f spectral density. XPS and BIS of U intermetallics[2-4] indicate that not all spectral features can be understood as pure bandlike, and especially the BI spectra show a coexistence of bandlike and localized $5f$ signatures. Because of the similarities between the Ce and U materials, a possible starting point is to describe U intermetallics within the Gunarsson-Schönhammer model.[5] However, a Ce-style single-impurity model has serious limitations in U intermetallics, where the peak close to E_F in BIS (attributed to a Kondo resonance in the case of Ce) has finite intensity even for magnetic U intermetallics (see, for example, Ref. 3). The U $5f$-$5f$ interaction (albeit often involving an intermediate orbital) is stronger and not negligible. This has been a major tenet of the application of band theory to actinides.[6] It might be interesting to extend the periodic Anderson Hamiltonian to the U intermetallics,[4] but unfortunately no derivation yet exists of its spectroscopic properties. Some progress can be made, however, if one assumes that the hybridization is sufficiently strong so that one can instead use a Hubbard model based on the formation of hybrid orbitals. In so doing, one is turning the problem around to look at materials where the f orbitals are strongly admixed into the band structure and then proceeding to materials with weaker admixture. Thus, in this Letter, we present XPS and BIS data for USi_3—a material with highly itinerant-electron behavior[7]—and UIr_3—a material that exhibits weak localized properties—as representative systems. By comparing with careful band-structure calculations we show that USi_3 is well described by a simple band description and that UIr_3 exhibits additional structures in BIS but not in XPS. A simplified treatment of the Hubbard model based on second-order perturbation theory[8] is used to suggest that this should indeed be the case for U intermetallics. This then has significant implications concerning the data for uranium metal where no additional structure is seen in the BIS yet a peak has been interpreted as a satellite in the occupied part of $5f$ structure.[9]

USi_3 and UIr_3 crystallize in the Cu_3Au structure which has been suggested as a basis for systematic studies.[6,7] Their U-U separations (4.035 and 4.023 Å, respectively) are much larger than the Hill limit of 3.6 Å.[10] Direct U $5f$-$5f$ overlap is negligible in this case. These would have magnetic ground states were it not for the strong f-p and f-d bonding consistent with USi_3 and UIr_3 being Pauli paramagnetic. As a consequence, the Wannier orbitals that underly the application of a Hubbard model must be hybrid orbitals which lead to increased hopping integrals and decreased Coulomb integrals. We shall not describe the details of the band-structure calculations here beyond mentioning that they are improved self-consistent results using the Hedin-Lundqvist exchange-correlation functional and at no stage omitting the spin-orbit coupling.

In order to compare the experimental spectra with the calculated partial density of states (PDOS), the latter has been broadened by folding the resolution function of the spectrometer. It has been further broadened with an energy-dependent Lorentzian function having a FWHM of $0.1(E-E_F)$, where E is the energy below the Fermi energy, E_F. Experimental details are given elsewhere.[2]

The previous resonant photoemission study[11] on UIr_3 found that the U 5*f* states below E_F clearly show a band signature, which was further supported by the observation of dispersion in the 5*f*-related features. All features observed could be satisfactorily explained from the *f* PDOS. The XPS valence band of UIr_3 is dominated by Ir *d* states as a result of differences in cross sections[12] and we shall not discuss it any further here. In USi_3 the XPS valence-band spectrum is expected to be primarily due to U 5*f* states. In Fig. 1 we show the XPS valence band of USi_3 compared to the broadened U 5*f* PDOS. We find good overall agreement between the experimental spectrum and the calculated one, and thus the observed spectrum is attributable to band-structure effects. We conclude that in these compounds the occupied part of the U 5*f* states is satisfactorily described by the PDOS within a (ground state) single-particle approximation.

In Figs. 2(a) and 2(b) we show the BI spectra of USi_3 and UIr_3. Differences in cross sections indicate that the BI spectra in these compounds are dominated by the U 5*f* states.[12] A few general remarks can be made about the BIS of these two compounds. In both materials, there is a large intensity signal just above E_F with its maximum at around 1.2 eV. USi_3 exhibits a fairly sharp peak at 1.2 eV with a weak shoulder at 0.6 eV. This shoulder is much stronger for UIr_3, which also shows the main peak at 1.2 eV. Moreover, USi_3 shows a weak feature at about 2.7 eV and UIr_3 exhibits a peak at about 3 eV. (Similar features about 3 eV above E_F have also been reported for UPt_4Ir,[2] $UNi_{5-x}Cu_x$,[3] and UPt_3.[4])

We first compare the BI spectrum of USi_3 to the broadened U 5*f* PDOS. The BIS of USi_3 is seen to correspond well to the itinerant-electron band results including the feature at 2.7 eV. In UIr_3, we should include the effects of the Ir *d* states, but the calculated Ir *d* PDOS (not shown here) indicates that the Ir *d* states contribute weak intensity only very close to E_F and thus cannot explain the feature at 3 eV. The main peak of UIr_3 BIS including features at 0.6 and 1.2 eV agrees quite well with the calculated *f* PDOS. Comparison to the *j*-projected PDOS shows this to be due to the spin-orbit splitting of the $f_{5/2}$ and $f_{7/2}$ states. It is not seen in USi_3 because the greater hybridization has washed it out. In the introduction we indicated that the bandlike signature of U 5*f* states close to E_F in magnetic U intermetallics cannot be attributed to the Kondo-resonance peak in analogy to the BIS of nonmagnetic Ce compounds. The excellent agreement between the calculated *f* PDOS and the XPS and BIS

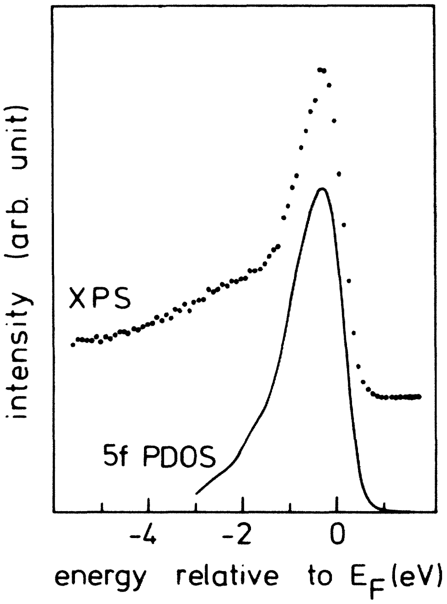

FIG. 1. XPS of USi_3 compared to the calculated 5*f* PDOS after broadening.

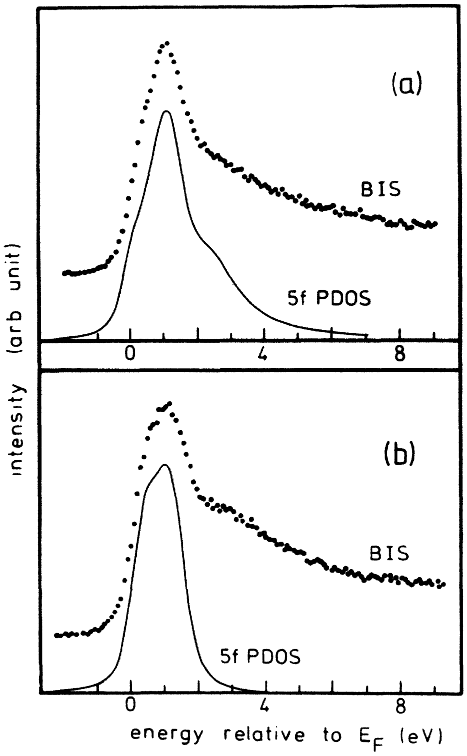

FIG. 2. BIS of (a) USi_3 and (b) UIr_3 compared to the calculated 5*f* PDOS after broadening.

of these nonmagnetic compounds also argues against the invoking of the Kondo-resonance peak in analogy to Ce for the nonmagnetic U intermetallics as well.

The new aspect is that the structure at 3.0 eV of UIr_3 is not seen in the band results (unlike the 2.7-eV structure in USi_3). We refer to this extra feature observed in the BIS of UIr_3 as a satellite, since it does not appear in the ground-state band structure. Similar satellites, as seen here for UIr_3 BIS, have recently also been observed in the $UNi_{5-x}Cu_x$ alloy system[3] where, by varying of the composition, it was shown that the relative intensity of the satellite increases with decreasing hybridization of U $5f$ states and with the concomitant increasing tendency to magnetic behavior. The convolution of a satellite considerably removed from E_F with a band signature around E_F is a situation similar to the XPS valence band of Ni,[13] where the satellite has been interpreted in terms of quasilocalized two-hole d-level bound-state formation. One important difference between Ni case and the U intermetallics is that the satellite appears in the XPS for Ni and in the BIS for U compounds. This is perhaps consistent with the fact that the Ni d levels are almost full and the U f levels are almost empty. Since numerous calculations incorporating the d-band correlation effects[14] are available for the Ni XPS, this analysis suitably modified can be used for the U intermetallics. Here we adopt the simplest Hubbard Hamiltonian model where the self-energy is evaluated by a perturbation expansion through second order in U/W (U is the Coulomb integral; W is the bandwidth).[8]

Since we are only interested in the qualitative trends observed in the spectra, we assume a rectangular DOS for the f electrons and examine the effect of the Coulomb integral (U) on this DOS. The Fermi level has been placed in the rectangular DOS such that the occupancy is $\frac{3}{14}$ and the degeneracy of the f level (14) has been taken into account. The results of the model calculations for several values of U/W are shown in Fig. 3. With increasing U/W, the occupied part of the DOS is only slightly distorted, whereas a clear satellite appears in the unoccupied part of the spectra ($E > E_F$), indicating that the satellite should indeed be expected to appear in the BIS and not in the XPS. Consequently, this satellite in BIS of U intermetallics can be attributed to the formation of a two-electron bound state. In support of this interpretation, such a two-electron bound state has successfully been calculated for a Ce compound (CeP).[15] If one uses a value for W representative of the $5f$-band width in UIr_3 (instead of 1 eV in the present model calculation), the satellite would appear at higher energy (~ 3 eV), in agreement with the experimental result. The proposed model describes the qualitative trend very well.

The substantially increased f-band width of USi_3—which at the same time implies a decreased U—dictates the absence of any strong satellite through too small a value for U/W. The increasing intensity of the satellite with increasing U/W (Fig. 3) is consistent with the experimentally observed trend to higher satellite intensity with decreasing U ligand hybridization that is characteristic of the magnetic materials.[3]

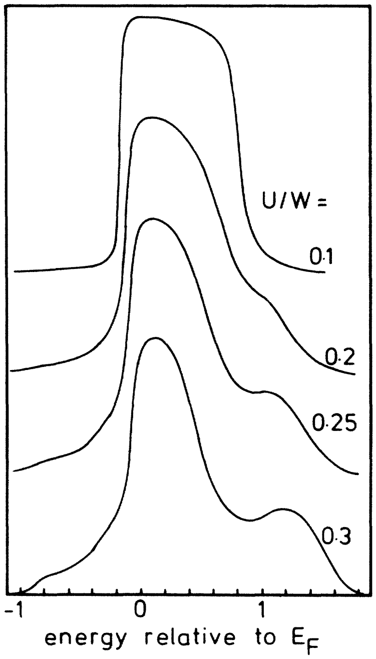

FIG. 3. Spectral weight of a rectangular DOS having a width $W=1$ eV and Coulomb correlation U for different values of U/W, within the model calculations (see text).

Note that the value of U is considerably smaller than that normally assumed for uranium (~ 2–2.5 eV). This is consistent with the Hubbard model being for hybrid orbitals which have significant density on the other (i.e., nonuranium) atom. The resulting expanded size of this hybrid orbital must result in a reduced Coulomb integral.

These results also have implications for the interpretation of the data available on uranium metal. It has been suggested that uranium should exhibit an XPS satellite.[16] Structure was reported for a synchrotron study of U metal at about 2.5 eV below E_F and interpreted as the satellite.[9] An alternative explanation has been proposed that the observed feature is really due to the uranium d electrons and not due to correlation effects.[17] The result for $U/W=0.3$ shown in Fig. 3 exhibits the presence of a weak satellite in the XPS as well. This suggests that at U/W values (>0.3) for which an XPS satellite would be observed, the BIS satellite would be quite pronounced. However, no BIS satellite has been observed in uranium metal indicating that the existence of an XPS satellite is highly improbable.

In conclusion, we have shown that the spectral features of these U intermetallics can be understood as starting from the underlying band structure plus the appearance of a two-electron bound state in BIS. The intensity of this satellite increases with increasing U/W leading to larger satellite intensities for the more correlated materials. Because this is also the criterion for the formation of a magnetic ground state, the larger satellite intensity correlates strongly with the tendency for magnetism.

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