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Characterization of the hybridized 4*f* states in $YbAl_3$ by high-energy spectroscopies

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The intermetallic compound $YbAl_3$ has been studied by bremsstrahlung isochromat spectroscopy, x-ray photoemission, and high-resolution (<20 meV) uv photoemission using He I and He II lines. The spectra analysis with the Anderson single-impurity model for $T=0$ reveals a ground state with an important hybridization of *f* states with band states, corresponding to an *f* population $n_f=13.5$. In contrast to all investigated metallic Ce systems which are in the Kondo regime, $YbAl_3$ is found to be in the mixed-valence regime. A rough calculation provides an explanation for the comparable hybridization strengths observed in Ce and Yb systems.

During the last decade special attention has been devoted to the lanthanide systems showing manifestations of the Kondo effect, of heavy fermions and of mixed valence.[1-3] It is now generally accepted that the origin of these unconventional properties must be looked for in the weak coupling between the atomiclike 4*f* states and the band states of the solid. The particular mechanism responsible for the ground-state stability of these systems is rather directly reflected by their excitation spectra within the low-energy range defined by the total energy lowering δ which results from the hybridization.[4] For Ce systems only, photoemission spectra have been recorded with a sufficiently high resolution to give access to these low-lying excitations.[5-7] Their analysis within the single-impurity model appeared to be compatible with the low-temperature specific heat.

Heavy lanthanides also show unusual properties originating most likely from the same hybridization mechanism. Yb compounds offer a situation perfectly analogous to the one met in Ce or La, if the role of occupied and empty 4*f* states is interchanged and the energy scale inverted.[8] This mirror property of Ce and Yb systems allows us to use exactly the same single-impurity model in both cases. However, for Yb the values of the parameters defined in this model may be different from those characterizing the Kondo limit found for Ce, so that one can hope to verify experimentally the existence of one of the other regimes predicted by this theory.[9-11]

The intermetallic compound $YbAl_3$, displaying puzzling properties, was chosen for this investigation. From the lattice constant which fits fairly well in the systematics of the trivalent heavy rare-earth aluminides,[12] one could conclude that the Yb ions are very close to the magnetic trivalent configuration. However, at low temperatures the magnetic susceptibility does not follow the Curie law expected for this configuration.[12] An anomalously large coefficient of the specific heat has been reported,[12] suggesting an *f*-symmetry admixture to the Fermi surface. Mössbauer isomer shift measurements showed that the valence of Yb in $YbAl_3$ has no temperature dependence and a fractional value of 2.7 was obtained from the data analysis.[13] X-ray photoemission spectroscopy (XPS) has revealed two sets of final-state *f* multiplets which were interpreted as originating from a ground state consisting of the two nearly degenerate $4f^{13}$ and $4f^{14}$ ionic configurations[14] fluctuating in time.[15] Within this intuitive model of valence fluctuations, one of the characteristic symptoms revealing this situation in *f* photoemission spectra is the pinning at E_F of the lowest component of the $4f^{13}$ multiplets.[16] With the resolution currently achieved in XPS, the validity of this criterion seemed to be verified many times. However, photoemission spectra of $YbAl_2$, taken at $h\nu=70$ eV with a resolution of 170 meV, showed that the first *f* component is not located at E_F but 240 meV above it.[17] This unexpected observation has been tentatively attributed to some incomplete relaxation of this photoemission final state.[17] The different results obtained for Yb systems can be hardly reconciled with conventional arguments and there is an urgent need for a unified description of their properties. The aim of the present Communication is to show that the observation of the low-energy excitations with high-resolution photoemission yields a decisive contribution to this problem.

The polycrystalline $YbAl_3$ sample was grown from Al flux in an evacuated Al_2O_3 tube. An x-ray analysis confirmed the single-phase cubic Cu_3Au-type structure of the sample.[12] The electron spectroscopic measurements were performed in an apparatus combining x-ray photoemission spectroscopy (XPS), bremsstrahlung isochromat spectroscopy (BIS), and uv photoemission spectroscopy (UPS) excited with the two narrow He I and He II resonance lines at 21.2 and 40.8 eV.[5] The total instrumental resolution of these techniques was 0.3, 0.4, and <20 meV, respectively. The sample was cooled to about 25 K using a closed-cycle He refrigerator in order to sharpen the Fermi edge and to prevent oxygen diffusion from the bulk to the surface. The contamination could be maintained below the limit of detection by frequently scraping the sample with an Al_2O_3 file.

The analysis of the spectra has been performed within the single-impurity model. Advantage was taken of the mirror property of Ce and Yb systems previously mentioned to carry out a Gunnarsson-Schönhammer (GS)-type calculation[4] of the spectral function at $T=0$. It included the $4f^{14}$ configuration and the $4f^{13}_{7/2}$ and $4f^{13}_{5/2}$ states separated by 1.26 eV (Ref. 18) but could not take into account the $4f^{12}$ configuration, which is about 8 eV above the ground state. In the hole language, it is convenient to define ε_f as the total energy difference between the two lowest unhybridized $f^{13}_{7/2}$ and f^{14} configurations and this parameter has a negative value since without hybridization $f^{13}_{7/2}$ would be the ground state of $YbAl_3$. The coupling strength between f and band states is taken into account by the parameter Δ.[4] The band is simulated by a Lorentzian of 6 eV full width at half maximum (FWHM) and centered 2 eV above the Fermi level. In order to still obtain an estimate of the $4f^{12}$ contribution (without multiplet splitting) to the final states, a much simpler calculation in the zero-bandwidth limit[19] has also been performed.

Figure 1 displays the XPS (a) and BIS (b) spectra recorded at 25 K and the corresponding single-impurity calculations for $T=0$ (c), (d). In the XPS spectrum the $4f^{12}$ final-state multiplets are clearly recognized between 5 and 11 eV below the Fermi energy. Near E_F two narrow peaks are observed with an energy splitting of 1.2 eV and an intensity ratio of about 8:6. These observations allow us to identify them with $4f^{13}_{7/2,5/2}$ final states as encountered in Yb-metal[20] but shifted by ≈ 1 eV towards E_F. Spectra taken at room temperature (not shown here) display an enhanced $4f^{12}$ multiplet intensity already observed in XPS spectra of $YbAl_3$ (Ref. 14) and $YbAl_2$.[21] For $YbAl_3$ this excess of intensity could be widely reduced by cleaning the sample surface so that we attribute it to the occurrence of the $4f^{12}$ multiplets of Yb oxide formed by oxygen diffusion from the bulk to the surface region of the sample. The measurement of the BIS spectrum shown in Fig. 1(b) required a particular care since even at low temperature the electron beam induced a fast formation of Yb oxide immediately detected as a $4f^{14}$ final state about 1.5 eV above E_F. The first peak at E_F is less pronounced than in the BIS spectrum of $YbAl_2$;[21] therefore, in accordance with the stoichiometry difference, we identify it with f emission while the broad maximum extending towards higher energies is attributed to the emission from band states.

Figure 1(c) displays the zero-bandwidth model calculation for XPS where the $4f^{12}$ spectral weight is concentrated in a 2 eV FWHM Lorentzian since multiplet splitting has been discarded. All other structures are broadened by Lorentzians of 0.3 eV FWHM to account for the instrumental resolution. The values of the different parameters has been chosen in such a way that the calculation reproduces the $I(4f^{13})/I(4f^{12})$ intensity ratio. The ground-state f occupation n_f is found to be 13.4. For U_{ff}, the value of 7 eV corresponding to the center of gravity of the $4f^{12}$ multiplet is roughly the same as found in most Ce systems.[22] The calculation for the BIS spectrum, also shown in Fig. 1(d) will be discussed below.

In order to obtain detailed information concerning the low-energy excitations, high-resolution uv spectra were recorded [Figs. 2(a)–2(d)]. At these low photon energies, however, photoemission becomes extremely surface sensitive, as demonstrated by spectra (a) and (c). By comparison with the spectra of Yb metal[23,24] and $YbAl_2$ (Ref. 17) the structures at 1.2 and 2.4 eV are identified as origi-

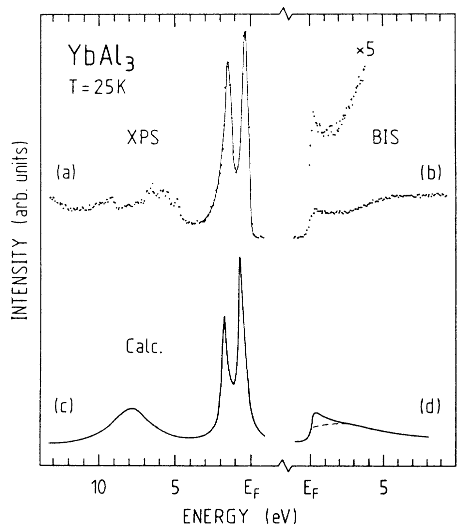

FIG. 1. (a) XPS and (b) BIS spectra of $YbAl_3$. (c) Simulation of the f-photoemission spectrum within the zero bandwidth approximation. (d) Simulation of the BIS spectrum by a GS calculation of the f excitations superimposed on a Lorentzian band (dashed line).

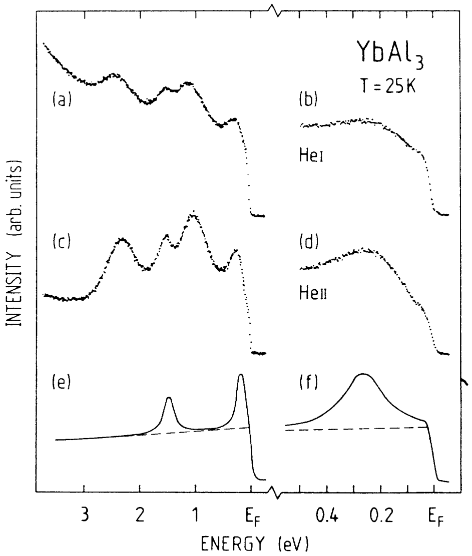

FIG. 2. (a)–(d) uv-photoemission spectra of $YbAl_3$; (a), (c) in the full range of surface and bulk $4f$ excitations; (b), (d) in a narrow energy range above E_F. (e), (f) Calculation simulating the bulk contribution to the spectra (c) and (b) (see text).

nating from divalent Yb ions ($4f^{14}$ configuration) present at the surface where the coordination is different.[25] The bulk $4f$ emission is recognized near E_F and at 1.5 eV, in agreement with the peak positions observed in the much less surface sensitive XPS spectrum [Fig. 1(a)]. In the low-energy flank of the first peak near E_F a weak shoulder reveals the Fermi edge; therefore, the energy region of this peak has been measured in detail. The resulting spectra displayed in Figs. 2(b) and 2(d) illustrate the enhancement of the cross-section ratio between $4f$ and band states when the photon energy increases and demonstrate unambiguously that the top of the f emission peak is located at 240 meV and not at E_F.

Figures 2(e) and 2(f) display the calculated f-photoemission spectra of the bulk (solid curve above the dashed line) computed within the GS model. The contribution from the band states (dashed line) is adjusted to give the best agreement with He II experiment. In this model calculation the experimental position of the first peak is obtained for the parameters $\Delta = 80$ meV and $\varepsilon_f = -0.2$ eV yielding a ground state which contains an f population $n_f = 13.6$ and is lowered by $\delta = 240$ meV with respect to the uncoupled $4f^{13}_{7/2}$ state. Since for a zero bandwidth the simple model underestimates n_f and by omission of the $4f^{12}$ configuration the GS model overestimates n_f, a value of 13.5 seems reasonable for $\mathrm{YbAl_3}$. The agreement between measured and calculated spectra is gratifying but not quite perfect. The fact that the experimental spectrum is broader than the simulated one is not surprising since lifetime broadening and electron-hole pair excitations are not included in the model. With the same parameters we have calculated the f spectral function for BIS. The result shown in Fig. 1(d) includes the contribution of the band estimated from XPS and is broadened by the experimental resolution of 0.4 eV. The total f contribution, normalized with respect to XPS by the factor $(N_f - n_f)/n_f = 1/27$, is essentially the continuation of the tail of the $4f$ photoemission peak. The comparison with experiment shows that this f signal superimposed to the emission from band states can only be discerned near E_F.

It is now instructive to contrast this spectra analysis of $\mathrm{YbAl_3}$ with those performed previously for different metallic Ce systems.[5-7,26,27] In these latter it has always been found $-\varepsilon_f \gg \Delta$, with ε_f between -1 and -2 eV and Δ of the order of 50 to 150 meV. These conditions are typical for the Kondo regime in which the f population n_f is very close to the integral value 1 and the energy lowering δ ranges from < 1 meV in heavy-electron systems like $\mathrm{CeCu_6}$ (Ref. 26) to 25 meV in α Ce.[5] In $\mathrm{YbAl_3}$ the value $-\varepsilon_f = 200$ meV is substantially smaller than for Ce systems while the hybridization strength Δ is of the order of $-\varepsilon_f$. It results a fractional hole number $n_f^h \approx 0.5$ far from integral values and an important energy lowering $\delta = 240$ meV. This energy gain of the ground state is very large compared to kT for $T < 300$ K so that no variation of n_f is expected in this temperature range. Within the single-impurity model the condition $-\varepsilon_f \approx \Delta$ characterizes the mixed valent regime[9-11,28] which appears to be rather different from the oversimplified concept of configuration fluctuation proposed earlier to explain photoemission spectra showing distinct features of two $4f$ populations. In fact, the photoexcitation induces transitions to a low-energy continuum of final states starting at the Fermi energy identified with the ground state with $n_f = 13.5$. Towards higher energies this continuum transforms gradually into a practically pure $4f^{13}_{7/2}$ state at the first peak maximum. At 1.5 eV appear the final states attributable to the $4f^{13}_{5/2}$ component and between 5 and 11 eV to the $4f^{12}$ multiplets. This interpretation of the photoemission spectrum shows that the total energy lowering resulting from the hybridization is directly given by the energy position of the $4f^{13}_{7/2}$ peak referenced to the Fermi energy.

The present interpretation of the electronic structure of $\mathrm{YbAl_3}$ rests exclusively on the analysis of the outer level spectra. The reason for this is twofold: (i) the $3d$ levels usually considered are not accessible with the Al $K\alpha$ line in Yb and (ii) the spectra of the less bound $4p$ and $5p$ levels[29] display a very rich multiplet structure (not shown here). The interpretation of such spectra would require a GS calculation including as basis states all possible atomic multiplets. This is a difficult task that we have not attempted since it would add to our otherwise complete spectra analysis only the determination of the Coulomb energy U_{fc} between a core hole and an f electron.

The formal analysis of the excitation spectra of $\mathrm{YbAl_3}$ within the single impurity model appears to be very successful. However, the comparable magnitude of the coupling strengths Δ in Ce and Yb systems is totally unexpected if only the $4f$ wave-function contraction across the lanthanides is considered. In simple molecular orbital theories the coupling strengths are often taken to be proportional to the corresponding overlap matrix elements. We have estimated the overlap matrix elements S between an f orbital and plane waves at the Fermi energy of a jellium corresponding to the electron density of aluminum. In this approximation we used the $kr \rightarrow 0$ asymptotic form of $j_3(kr)$, representing the f-partial wave in the plane-wave expansion around the Yb nucleus. We find $S(\mathrm{Yb}, n_f = 13) = 5.4$, $S(\mathrm{Yb}, n_f = 14) = 44$, $S(\mathrm{Ce}, n_f = 0) = 6.7$, $S(\mathrm{Ce}, n_f = 1) = 24$. This behavior of the overlap integrals originates from the tails of the $4f$ wave functions, which in both cases become more intense when the potential is weakened by an f-count increase. Starting from trivalent configurations where the tail is weaker for f^{13} than for f^{1}, the hybridization induces a positive variation of n_f in Yb and a negative one in Ce. If this relative population change is large enough (as in $\mathrm{YbAl_3}$) it can cancel the intensity difference of the tails obtained in the pure trivalent configurations. This mechanism is likely to explain the occurrence of similar hybridization strengths in Ce and Yb systems.

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