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Resonant photoemission from $Ce_{24}Co_{11}$ at the 4*d*-4*f* threshold

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Angle-integrated photoemission spectra from $Ce_{24}Co_{11}$ are presented in the region of the 4*d*-4*f* threshold (112–130 eV) and are interpreted in the frame of the impurity model. The constant-initial-state spectra with initial states in the two photoemission structures having 4*f* character (near the Fermi level and at −2.1 eV) are different across the 4*d*-4*f* resonance. The impurity model including 4*d* core levels of Ce gives excellent fitting of the constant-initial-state spectra; the dependence of the results on the parameters of the model is discussed.

Resonant photoemission across the so-called giant resonance at the 4*d*-4*f* threshold has emerged as a very powerful tool to understand the electron states of rare earths. In the Ce compound this approach has been shown to be particularly useful for enhancing the signal due to the ionization of the 4*f* level. This gave relevant information as discussed in detail in Ref. 1; in particular, it has been possible to distinguish easily between systems having different intensities of the so-called Kondo-like behavior. In this connection the purpose of this Brief Report is twofold.

(i) The presentation of the results for $Ce_{24}Co_{11}$—a compound which to our knowledge has not been investigated with synchrotron radiation and in particular with resonant photoemission. This choice is significant because this compound is not yet completely investigated [for x-ray photoemission spectroscopy (XPS) see Ref. 2] and because it belongs to the Ce-rich side of the Ce-Co phase diagram; in the case of a Co-rich compound such as $CeCo_2$, resonant photoemission data are available[3] so that this report completes the data on the Ce-Co phase diagram.

(ii) The discussion of the shape of the spectra taken in the constant-initial-state (CIS) mode across the 4*d*-4*f* threshold. This is done in connection with a theoretical treatment[4] which extends to resonant photoemission the treatment by Gunnarsson and Schonhammer[5] based on the Anderson impurity Hamiltonian [Ref. 4 will be referred to as T (theory) and is supposed to be known to the reader]. This is the first comparison between the theory of Ref. 4 and experiment. We will show that this treatment gives satisfactory shapes for the CIS spectra.

These two issues are treated successively after the presentation of some experimental details.

The samples were prepared as described in Ref. 6 and were characterized with x-ray diffraction. The surface was cleaned *in situ* by scraping with a diamond file; the base pressure in the experimental chamber was 7×10^{-11} Torr, and no signal from contaminants was found with photoemission. The measurements were performed at the "old grasshopper" beamline at SSRL (Stanford Synchrotron Radiation Laboratory) with a cylindrical mirror analyzer (CMA); the light was incident about 15° from the surface. The beam line was equipped with a device to monitor the flux (I_0) incident onto the sample and based on the total yield of a fine copper grid inserted in the beam (the total emission was measured with a channeltron with appropriate bias). The angle-integrated EDC's (energy distribution curves at constant $h\nu$) were measured at constant pass energy of the CMA (15 eV). The CIS spectra were measured directly on line by sweeping simultaneously the CMA (operated in the constant pass energy mode) and the monochromator; this has been done with steps of 0.2 eV. In the normalization to the I_0, the correction due to the $h\nu$ dependence of the Cu quantum yield and to the higher order from the photon spectrometer were done; the measured $h\nu$ dependence of I_0 was fully consistent with that measured in a separate run with a calibrated photodiode. Also, the correction for the energy dependence of the CMA efficiency was done.

The effect of the above corrections is small because of the limited photon energy range interesting for the present discussion (typically 112–130 eV).

The photoemission spectra (EDC's) are collected in Fig. 1 (left panel) where we report the spectrum at 112 eV (i.e., below the $4d$-$4f$ threshold) and a collection of closely spaced spectra across the resonance. The modification of the spectra at resonance is quite evident, and the assignment of the features is straightforward and analogous to the other cases given in Ref. 1. The features near the Fermi level E_F and at -2.1 eV are due to the ionization of the $4f$ electron and correspond to two different final states: The first, which includes also the so-called Kondo peak, has dominant f^1 character, while the other has f^0 character. These features resonate across the $4d$-$4f$ threshold. Most of the contribution to the spectra in the region between these features comes from the d-derived states; of course, some d character is also spread in the region of the two features.

The comparison between the spectra at resonance and the spectrum off resonance (at 112 eV) allows the extraction of the $4f$ contribution as discussed in detail in Ref. 1; this requires the calculation of the difference spectra after normalization to the I_0 and correction for the $h\nu$ dependence of Co $3d$ photoemission cross section. To this end we have used the atomic dipole cross section of Ref. 7. This approach is safe since it has been demonstrated that solid-state effects on the $3d$ photoemission cross sections are marginal in this $h\nu$ range.[8] The inelastic background due to secondary electrons has also been subtracted from the EDC's; as usual, the background has been obtained from the integral of the spectrum from the current energy to the end point.

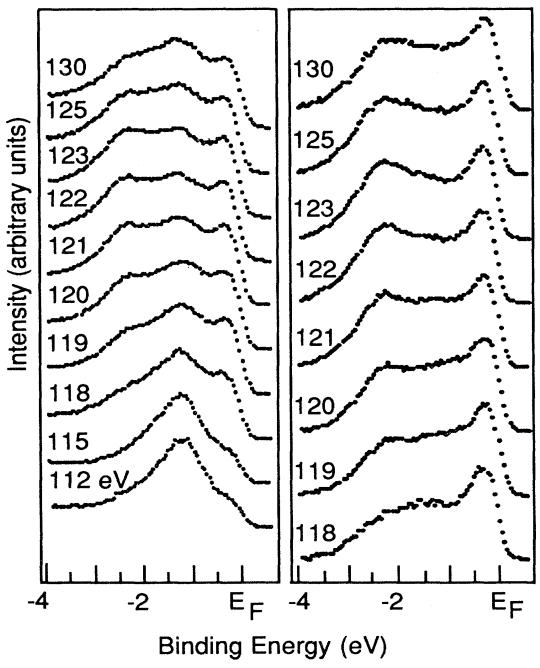

FIG. 1. (Left panel): Angle-integrated photoelectron spectra from $Ce_{24}Co_{11}$ in the region of the $4d$-$4f$ resonance (the label is the photon energy in eV). (Right panel): $4f$ "extracted spectra" obtained from the measurements of the left panel as explained in the text (the label is the photon energy in eV); the inelastic background has been subtracted.

The results are given by the so-called "extracted $4f$ spectra" presented in Fig. 1 (right panel) where the spectra have been normalized to the same height in order to point out the shape variation. The extracted spectra show clearly that the f^1 peak resonates before the f^0 peak; this effect seen for the first time in $CeSi_2$, and in CeAl (Ref. 9) is connected with the different configurations involved in the two channels and is accounted in T as shown below.

In the region where both features resonate, the intensity of feature f^1 is slightly greater than that of feature f^0; this is interesting because the relative weight of the two features is in general very much dependent on the nature of the compound as pointed out in Ref. 1. As a matter of fact, there is a whole range of variation from a more pronounced Kondo-like behavior as in $CeNi_5$ with the upper feature at E_F more pronounced to a case as $CeSi_2$ where the feature at E_F is much smaller than the other (we refer to the spectra taken at room temperature presented in Ref. 1). The present results show that $Ce_{24}Co_{11}$ is in an intermediate case between the two extremes.

In the "opposite" stoichiometry ($CeCo_2$ reported in Ref. 1), the extracted $4f$ signal is similar to the present one with a marginal increase (20% within the experimental errors) of the relative weight of the f^1 feature with respect to the present case, suggesting a slightly greater hybridization in $CeCo_2$ than in $Ce_{24}Co_{11}$. The similarity of the two compounds in terms of hybridization is to be taken as an experimental result since there is no immediate argument to draw this conclusion from the structures of the two compounds, which have quite different symmetries and atomic coordination (see Ref. 10); however, we could reasonably expect a somewhat larger value of the hybridization in Co-rich compounds since the coupling to the Co $3d$ band might be more efficient.

The extracted $4f$ spectra can be used in conjunction with the $4f$ spectra calculated at resonance (see T) and with the XPS results of Ref. 2 to discuss the order of magnitude of some relevant parameters in the Anderson Hamiltonian. The calculations of the photoemission spectra reported in T (Fig. 6) suggests that the hybridization parameter $N_f\Delta$ (where N_f is the degeneracy of the $4f$ levels) is greater than 0.7 eV since this value gives a too small f^1 feature in the spectra above the maximum of the resonance [typically, consider the case $\omega=3$ eV of Fig. 6 in T (Ref. 11)]. The XPS $3d$ spectra are very useful in this connection; we have fitted the $3d$ spectra of $Ce_{24}Co_{11}$ given in the previous work,[2] obtaining $N_f\Delta=1.2\pm0.1$ eV (Ref. 12) (the XPS spectra of Ref. 2 are not reported here for space reasons). Going back to the comparison with $CeCo_2$, the similarity of the behavior is confirmed by the fitting of $CeCo_2$ with the Anderson impurity model done for $3d$ photoemission in Ref. 13: In $CeCo_2$ this parameter is estimated to be 1.7 eV, i.e., about 40% stronger than in our case, consistent with what we have guessed from resonant photoemission.

The other relevant issue is the comparison with the

theoretical CIS spectra across the $4d$-$4f$ resonance based on the treatment given in T.

To this end we use the measured CIS spectra by noting two points. (i) The comparison between theory and experiment is centered on the CIS shape (initial states at -0.3 and -2.1 eV) since the comparison cannot be extended to the resonance intensities defined as the ratio of the counting rate at the resonance and before the resonance. This is due to the CIS background coming from states other than the $4f$; in the experiment this contribution is mostly due to photoemission from d-derived states, and its intensity cannot be described in a fully realistic way by the photoemission contribution from the elliptic conduction band assumed in the theory.[14] (ii) In principle, the measurement of the shape of the f^0 CIS can be influenced by the inelastic background coming from the f^1 feature. This correction can be evaluated in a reliable way by considering the integral background of the EDC's and the much smaller resonance of the mostly d peak at about -1.1 eV whose CIS has been measured to this purpose; this CIS gives also the resonance of the background associated with the the states lying between the $4f$ features. The final correction is basically negligible as far as the CIS shape is concerned; it has only a little effect on the onset of the f^0 CIS. For logical internal consistency we will use the CIS including this correction whose effect is hardly visible within the resolution of Fig. 3 reported below.

The theory (T) explains the delayed onset of the f^0 feature shown in Fig. 1. To this end it is essential to include in the calculations both the intermediate f^2 and f^3 configurations having different coupling to final states; the intermediate f^2 state couples strongly to the deeper peak (f^0), while the f^1 structure couples both to f^2 and f^3 intermediate states. We will show that already a qualitative comparison with the experiment is beneficial to point out the most appropriate region in the parameter space of the model.

In order to compare T with the experiment, it is convenient to proceed in two successive steps. Initially, we concentrate on the shape of the resonance for a single feature (the f^1 one), and next we discuss the differences between the two CIS spectra.

We have carried out a set of new calculations with the hybridization given above ($N_f\Delta=1.2$ eV); we did not use the theoretical CIS spectra of T since they refer to an hybridization parameter ($N_f\Delta=0.88$ eV) not appropriate for the present case. As a starting point, we used a reference case with the other parameters similar to those of T and precisely: $U_{fc}=-8$ eV, $\varepsilon_f=-1.6$ eV, $\Gamma_1=0.2115$ eV [i.e., $(N_f-1)\Gamma_1=2.75$ eV], $\tau_1/v_1=0.75$, $\Gamma_2=0$, $\gamma_2=0$, $\varepsilon_M^{(1)}=0$, $\varepsilon_M^{(2)}=20$ eV, $\varepsilon_M^{(3)}=18$ eV, and $\tau_c=0.2878$.

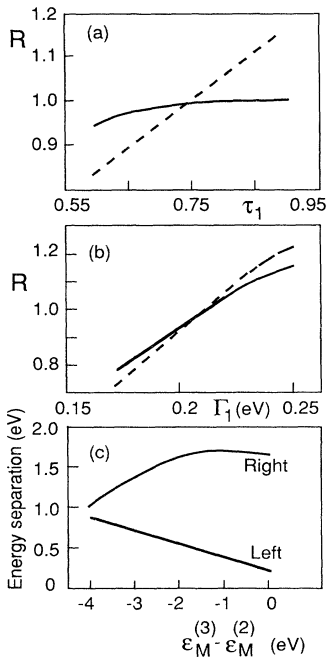

FIG. 2. Summary of the parameter effect on the shape of the $4d$-$4f$ resonance in the CIS spectra. (a) and (b) Left half-width of the resonance at half-height (solid line) and height of the resonance 8 eV above the peak measured with respect to the maximum height (dashed line). All values are expressed as dimensionless ratios R with respect to a reference case whose parameters are given in the text. (c) Energy separation between the edges of the two CIS spectra belonging to the f^0 and f^1 features in the photoemission spectra. The left edge is defined at half-height, the right at 70% height.

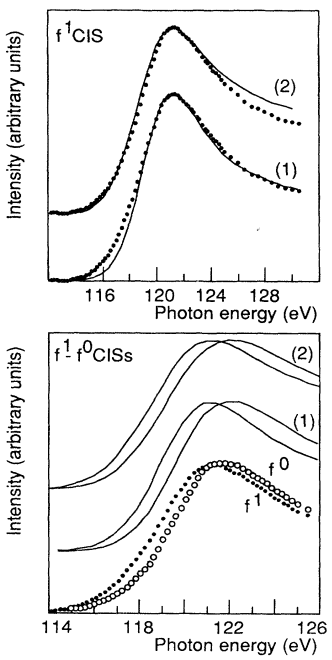

FIG. 3. Comparison between measured and calculated resonances. In the upper panel the f^1 CIS spectra are given: The circles give the measured f^1 CIS spectra (initial energy -0.3 eV), which is compared with the theory in cases (1) and (2) whose parameters are given in the text. In the lower panel both CIS spectra are considered [f^0, open circles (initial energy at -2.1 eV); f^1, solid circles]; for a better comparison with theory [cases (1) and (2)], a more expanded scale has been used in the lower panel. Experimental and theoretical CIS spectra are normalized to the same height.

At variance with respect to T, we have imposed in the calculation the condition $v_i\gamma_i=-\tau_i\Gamma_i$, which restricts the possible line shapes if we only consider one decay mechanism as in the present paper.

The good region in the parameter space was chosen with the following rationale based on the effects summarized in Fig. 2. In Figs. 2(a) and 2(b) we give the variation of the left half-width of the calculated resonance (solid line) and of the height 8 eV above resonance with respect to the maximum (dashed line) both measured in units of the reference case. In Fig. 2(a), τ_1 is varied at constant Γ_1, and in Fig. 2(b), Γ_1 is varied at constant τ_1. The parameter Γ_1 coming from a broadening operator increases the left width and weakens the resonance, i.e., has an effect both on the left and right of the resonance [Fig. 2(b)], whereas the greater τ_1 values increase the relative probability of direct photoemission, thus reducing the importance of the resonance with little effect on the left width (for a given τ_c) in the region of the parameter space covered in the present work.

On this basis one finds that a good combination of parameters to give the shape of the f^1 resonance is around the typical cases (1) $\tau_1/v_1=0.748$ and $\Gamma_1=0.2115$ and (2) $\tau_1/v_1=0.673$ and $\Gamma_1=0.25$. This is shown in Fig. 3 (upper panel). Both cases are satisfactory; case (1) is slightly better at the right while case (2) is very good at the left.

The separation between the two CIS spectra depends, as it is intuitive, on the energy separation of the intermediate states, i.e., on $\zeta=(\varepsilon_M^{(3)}-\varepsilon_M^{(2)})$. This dependence is given in Fig. 2(c), showing that the distance between the left edges (at half-height) of the two CIS spectra is linear in this parameter, over the parameter range considered here. However the two CIS spectra, belonging to two different interchannel couplings, are not rigidly displaced when ζ is varied; there is a distortion of the shape so that the distance between the right edges (at 70% of the height) has a different ζ dependence. The best agreement with the experiment is obtained for $\zeta=-2$ eV. The results are given in Fig. 3 (lower panel with a more expanded scale than in the upper panel) where the theoretical curves are compared with the experiment after scaling to the same height in order to focus on their shape (see above). The difference in the separation above the resonance in cases (1) and (2) is evident with an experimental indication in favor of case (2). The present theory does not give a Fano line shape[15] in general. However, if we assume that the initial state is a pure f^1 state and the intermediate state is a pure f^2 state and only one decay mechanism is included, a Fano line shape is obtained. The parameters then correspond to $q=1.8$ and 1.7 for the parameter sets 1 and 2, respectively.

In conclusion, we have presented resonant photoemission measurements on $Ce_{24}Co_{11}$ across the $4d$-$4f$ threshold and we have given an analysis based not only on the extracted $4f$ spectra, but also on the shape of the resonance. We have found the more appropriate parameters for the theory based on the impurity Hamiltonian, and we have discussed the sensitivity of the model to different parameters; a satisfactory fitting of the experimental results has been obtained.

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[11]In Fig. 6 of T, the zero photon energy for the theoretical spectra is the energy were the f^1 structure has its maximum; in the present measurements, this is 121 eV. Thus the spectrum at $\omega=-3$ eV has to be compared with the measurement at 119 eV; also, this comparison shows that the theoretical peak f^1 is too small since in the corresponding conditions the measured spectrum has a peak greater than f^0.

[12]In the previous work (Ref. 2), only an approximated value of $\Delta\cong 0.1$ eV (i.e., $N_f\Delta\cong 1.4$ eV) is given which is qualitatively consistent with the present argument.

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