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Correlation between the Kondo temperature and the photoemission spectral function in the $CeSi_x$ $(1.6 \leq x \leq 2)$ system

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In this paper, we study the evolution of the photoemission $4f$-electron spectral density as a function of concentration in the $CeSi_x$ $(1.6 \leq x \leq 2)$ system. The physical properties are strongly composition dependent around $x = 2$ reflecting large variations of the Kondo temperature with Si vacancies. Then this system represents an ideal case for photoemission investigations since it is possible to tune the Kondo temperature without significant changes of the non-f-electron density of states. Our spectroscopic measurements show a correlation between the Kondo temperature and the $4f$ intensity near the Fermi level as expected in the framework of the single-impurity Anderson model.

In the last decade, numerous studies using high-energy spectroscopies have given fruitful information on the $4f$ states in cerium-based heavy-fermion systems.[1,2] In particular, high-resolution $4f$ photoemission spectra exhibit the different energy scales corresponding to charge fluctuations, spin orbit, and crystal-field excitations expected from the single-impurity Anderson model (SIAM).[3] However, a recent resonant photoemission study of several Ce heavy fermion compounds claims that the $4f$ spectrum reveals several inconsistencies with the predictions of the SIAM:[4] (i) the width of the feature near E_F resulting from the Kondo resonance and its crystal-field sideband is too broad; (ii) no temperature dependence of the Kondo resonance is observed; (iii) there is no correlation between the spectral weight near E_F and the Kondo temperature. The suitability of the SIAM to describe the spectroscopic properties is then called into question. Our recent studies challenge this conclusion at least concerning the temperature dependence of the spectral density.[5,6] As the Kondo resonance is located above E_F in Ce compounds, we have investigated the evolution of the inverse photoemission spectra with temperature and we have shown that the $4f$ spectral density exhibits a temperature dependence reflecting the smearing of the Kondo resonance when temperature is larger than T_K. In this Rapid Communication, we investigate the third alleged inconsistency and demonstrate that there is an actual relation between the spectral weight near E_F and the Kondo temperature. In general, a quantitative study of this effect is difficult to perform because, even with $4f$ resonant photoemission, the states of other symmetries strongly contribute to the photoemission spectra and may prevent an accurate determination of the $4f$ signal. In order to avoid these difficulties, we have chosen to measure several $CeSi_x$ alloys. While the non-f spectral weight is expected to be weakly affected by the concentration of Si vacancies, the physical properties associated with the f states are known to be strongly composition dependent in this system.[7–10] $CeSi_2$ is a well-known heavy fermion with a nonmagnetic ground state corresponding to a Kondo temperature (T_K) estimated between 35 and 100 K; below $x = 1.80$ a ferromagnetic order appears around 10 K with a reduced magnetic moment, suggesting that the Kondo temperature drops with decreasing Si content.[6,7,11,12] Therefore, this system is especially appropriate to determine the modification of the *4f spectral density* accompanying the change of T_K.

$CeSi_x$ $(1.6 \leq x \leq 2)$, $LaSi_2$, and $CeGe_2$ samples were made by arc melting the constituent materials several times under argon atmosphere and they were characterized by x-ray powder diffraction patterns and magnetic measurements. $CeSi_2$ which crystallizes in the tetragonal α-$ThSi_2$ structure, admits a considerable amount of vacancies on the Si sublattice ($x \geq 1.75$) while still retaining its tetragonal symmetry.[9] Below $x = 1.75$ a distortion occurs and the alloys have the α-$GdSi_2$-type structure but this structural modification does not markedly affect the electronic and physical properties of the alloys.[9,10] The different spectroscopic measurements were performed in an apparatus combining ultraviolet photoemission spectroscopy (UPS), x-ray photoemission spectroscopy (XPS), and bremsstrahlung isochromat spectroscopy (BIS). The sample could be cooled with a closed-cycle He refrigerator to about 15 K. In UPS the overall energy resolution, estimated from the width of the Fermi step, is better than 20 meV. BIS spectra were obtained with a photon energy of 1486.6 eV and a total energy resolution of 0.6 eV was achieved. The pressure was in the low 10^{-10} Torr range during the measurements. The samples were cleaned by repeated scraping with a diamond file until no oxygen contamination (O $1s$ and O $2p$ photoemission signals) could be detected.

In Fig. 1, we report the He II ($h\nu = 40.8$ eV) photoemission (UPS) and inverse photoemission (BIS) spectra of $CeSi_2$ and $CeSi_{1.6}$. These spectra exhibit the characteristic features of the Ce-based heavy fermion compounds.[2] The UPS spectra are dominated by a broad structure near $E = -2.5$ eV reflecting the non-f valence-band states and the ionization peak of the Ce atoms ($4f^0$ final state). Near the Fermi level, the two additional well-resolved structures are predicted by the SIAM: the first one just below the Fermi level is interpreted as the tail of the Kondo resonance and the crystal-field excitations whereas the structure near $E = -0.3$ eV corresponds to

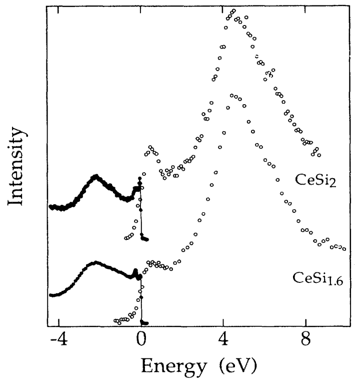

FIG. 1. He II photoemission and inverse photoemission spectra for $CeSi_2$ and $CeSi_{1.6}$ at $T = 15$ K.

the spin-orbit sideband.[3] In the BIS part, the structure located just above E_F represents the Kondo peak and its spin-orbit replicate (not resolved because of the poor BIS energy resolution) and the intense and broad feature between 4 and 7 eV reflects the multiplets of the $4f^2$ final state. In a hypothetical purely trivalent system, only the high-energy features ($E = -2.5$ eV in photoemission spectroscopy and $E = 4$–7 eV in BIS) corresponding to $4f^0$ and $4f^2$ final states, would be observed. Then, the spectral weight near E_F reflects the deviation from the trivalency and is roughly proportional to T_K.[13–15] The decrease of the near-E_F structures, clearly observed in both spectroscopies when lowering the Si concentration from 2 to 1.6, is fully consistent with the evolution of the Kondo temperature in the $CeSi_x$ system[7,10,11] and with the prediction of the Anderson model.

The quantitative comparison of experimental and theoretical spectra would require a very accurate determination of the f contribution. The extraction of the photoemission $4f$ signal is a notoriously difficult problem in Ce systems, especially for the $4f^0$ structure which is very often obscured by non-f states. This is clearly illustrated in the Fig. 2 where comparison of $CeSi_2$ and $LaSi_2$ spectra shows that the Si derived sp band strongly overlaps the $4f$ contribution in the -1, -3.5 eV range. Since an accurate estimation of the f^0 structure is difficult, we shall focus our attention on the near E_F region (600 meV) and we shall discuss the evolution with composition of the spectra in this region. As $LaSi_2$ exhibits a structureless spectrum in this energy range (cf., Fig. 2), the two observed near-E_F structures in the different $CeSi_x$ alloys can be unambiguously attributed to f states.

Before presenting the composition dependence of the experimental spectra and their correlation to the Kondo temperature, we briefly recall the prediction of the SIAM. Noncrossing approximation (NCA) calculations of the spectral density in the infinite Coulomb interaction limit ($U_{ff} = \infty$) predict that the intensity of the Kondo resonance scales with T_K.[14] It has also been shown that, even with crystal-field interactions, the calculated intensity ratio between the structure near the Fermi level and the spin-orbit sideband varies with T_K.[3] As recently demonstrated,[16] a finite U_{ff} does not substantially modify this picture so that the near-E_F region should reflect the modification of the physical properties. In Fig. 3, we have reported raw photoemission spectra of $CeSi_2$, $CeGe_2$, and several $CeSi_x$ alloys measured at 15 K with $h\nu = 40.8$ eV. The corresponding spectra recorded at $h\nu = 21.2$ eV where the $4f$ cross section is strongly reduced do not show any evolution with composition. With decreasing Si content, the intensity of the shallower structure strongly decreases between $x = 2$ and $x = 1.75$ and saturates for smaller concentration whereas the -0.3-eV feature is weakly affected. In $CeGe_2$, the spectral weight associated with the Kondo resonance is not detectable but the intensity of the spin-orbit sideband remains significant. The photoemission data therefore indicate that the Ce ions are not purely trivalent in this material. This is not surprising because although $CeGe_2$ orders magnetically at 7 K with a nonreduced magnetic moment, specific-heat measurements show that the entropy at the transition temperature is slightly less than $R \ln 2$, suggesting a residual Kondo effect.[17] The progressive evolution of the $4f$ spectral density with composition is consistent with the prediction of the SIAM. In order to establish this correlation in a more quantitative way,

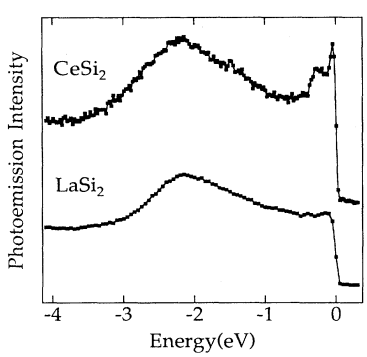

FIG. 2. He II photoemission spectra of $CeSi_2$ and $LaSi_2$ at $T = 15$ K.

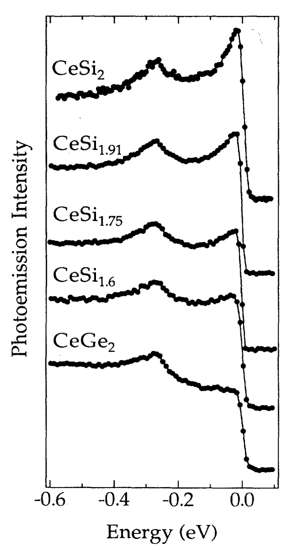

FIG. 3. High-resolution He II spectra at 15 K of the near-E_F region for several alloys of the $CeSi_x$ system and for $CeGe_2$.

we have estimated the intensity ratio between the structure near E_F and its spin orbit sideband as follows. The experimental spectra were fitted by superimposing two Lorentzians simulating the two $4f$ structures on a constant function representing the non-f states. The resulting curves were multiplied by a Fermi function. The phenomenological quantity plotted on the left-hand side of Fig. 4 is the intensity ratio of the two Lorentzians. We also report on the right-hand part of this figure the paramagnetic Curie-Weiss temperature (θ_p), estimated from the temperature dependence of the magnetic susceptibility in Ref. 10, which is known to be proportional to the Kondo temperature. A very good correlation between these two quantities is observed. The possible stabilization of more localized $4f$ states at the surface, recently observed in several cerium-based compounds,[18] could reduce the correlation between Kondo temperature and spectral weight. However the nearly quantitative agreement of estimations of T_K from photoemission and bulk techniques in $CeSi_2$ suggests that this surface effect is less prominent than in strongly hybridized materials like $CeIr_2$ or $CePd_3$ and can be ignored in the present $CeSi_x$ system. The evidence of a scaling between spectroscopic measurements and T_K contrasts with the results of Joyce *et al.*[4] which suggest that the $4f$ spectral weight is not correlated to the value of T_K. This discrepancy is a matter of debate and one could speculate that such a behavior could result from the difficulties to extract the $4f$ contribution and then to quantitatively compare $4f$ spectral weight in several materials with very different non-f density of states. Our results establish that, when the variation of the $4f$ signal near E_F can be extracted without ambiguity, it qualitatively scales with T_K in heavy-fermion compounds as expected from the Anderson model.

In this paper, we have investigated the modification of the photoemission spectral density as a function of composition in the $CeSi_x$ system. We show that the intensity of the near-E_F structure which partly reflects the tail of the Kondo resonance, strongly decreases with the concentration of Si vacancies and we verify the correlation between the relative intensity of the two near E_F $4f$ structures and the Kondo temperature. In contrast to recent claims,[4] our results unambiguously show that the evolution of the $4f$ spectra weight near E_F follows, at least qualitatively, the prediction of the Anderson model. To be more quantitative, an accurate determination of the whole $4f$ contribution is required to be compared with calculations of the $4f$ spectral densities. Efforts in this direction are in progress.

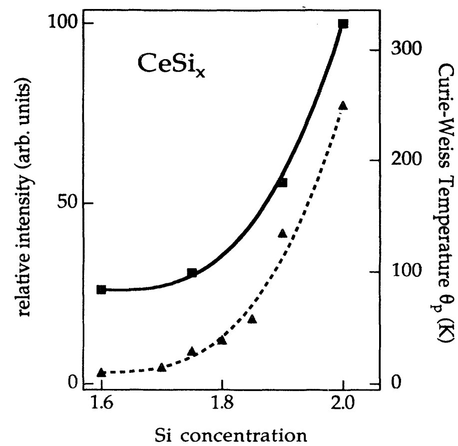

FIG. 4. Left-hand side (black squares): intensity ratio of the two Lorentzians (their widths are kept constant in the series) simulating the near-E_F structures; the solid line is a guide for the eye. Right-hand side (black triangles): evolution of the paramagnetic Curie-Weiss temperature (θ_p) as a function of stoichiometry from Ref. 10; the dashed line is a guide for the eye.

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