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Resonant photoemission studies of the Kondo-lattice systems $CeCu_2Si_2$, $CeAg_2Si_2$, $CeAu_2Si_2$, and $CePd_2Si_2$

R. D. Parks
Department of Physics, Polytechnic Institute of New York, 333 Jay Street, Brooklyn, New York 11201

B. Reihl
IBM Zurich Research Laboratory, CH-8803 Rüschlikon, Switzerland

N. Mårtensson
Department of Physics and Measurement Technology, Linköping University, S-581 83 Linköping, Sweden

F. Steglich
Institut für Festkörperphysik, Technische Hochschule Darmstadt, D-6100 Darmstadt,
Federal Republic of Germany

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Photoemission experiments performed at an incident photon energy of 70 eV provide a clear view of the transition-element-derived d bands in the systems CeT_2Si_2, with $T=$Cu, Ag, Au, and Pd. Spectra taken at $h\nu=122$ eV display both a resonant $4f$ emission at 2—3 eV below E_F, and a resonant emission near E_F. The total intensity of the latter feature, which has been observed in other Ce-based systems and identified as having strong $4f$ character in γ-cerium and $CeAl_2$, appears to track the intensities of the transition-element-derived d density of states near E_F. In superconducting $CeCu_2Si_2$, the E_F feature has its maximum at 0.25 eV, whereas we find it at significantly higher binding energies (~ 0.6 eV) in the three magnetic systems ($T=$Ag, Au, and Pd). This observation suggests markedly smaller electronic specific-heat (γ) values in the magnetic compounds as compared with $\gamma \simeq 1$ J mole^{-1} K^{-2} generated by heavy fermions in $CeCu_2Si_2$.

I. INTRODUCTION

The system RT_2Si_2, where R represents a rare-earth (RE) ion and T a transition- or noble-metal ion, includes a number of important archetypes in the mixed-valence and Kondo-lattice problems. For example, $EuPd_2Si_2$ is the only Eu-based system reported to exhibit a cooperative valence transition with temperature.[1,2] The Kondo-lattice system $CeCu_2Si_2$ is the only system reported to exhibit superconductivity in the presence of (and perhaps because of) heavy fermions generated presumably by interactions between the localized $4f$ electrons and the conduction electrons.[3,4] These systems crystallize in the tetragonal $ThCr_2Si_2$-type structure,[5] wherein the rare-earth atoms reside on planes well separated by layers of T and Si atoms.

Four particular members of the above systems, viz., $CeCu_2Si_2$, $CeAg_2Si_2$, $CeAu_2Si_2$, and $CePd_2Si_2$, were chosen for the present study because of previous characterizations which suggest that the nature of the $4f$ states and/or their hybridization with band states might vary significantly within this group. In both[4] $CeCu_2Si_2$ and $CePd_2Si_2$,[6] for which electrical resistivity measurements exhibit Kondo side-band resonances[7] and magnetic susceptibility measurements exhibit Curie-Weiss behavior, it appears that the energy of the Kondo-type fluctuations is either larger than or at least comparable to the energy of the cooperative transition, i.e., the onset of superconductivity at $T\sim 0.5$ K in $CeCu_2Si_2$ and the onset of antiferromagnetism at $T\sim 10$ K in $CePd_2Si_2$. On the other hand, in $CeAg_2Si_2$, which appears to undergo a ferrimagnetic transition at $T\sim 8$ K, and $CeAu_2Si_2$, which undergoes an antiferromagnetic transition at $T\sim 10$ K, there is no definitive evidence for Kondo-type fluctuations above the ordering temperature.[6]

Valence-band photoemission distinguishes itinerant electrons (by probing band structure) and emissions from localized (or quasilocalized) f electrons.[8] It has proved to be an important tool in the mixed-valence problem.[1] In mixed-valence Sm-, Eu-, Tm-, and Yb-based systems, which are archetypal promotional model systems,[9] valence-band photoemission experiments are capable of yielding directly the mixed-valence quotient of the ground state (see, e.g., Refs. 9 and 10). In these systems, the screened final-hole state $R^{3+}c^{n+1}$ in the photoemission process (where c is a conduction-band electron) is isoenergetic with the initial state $R^{2+}c^{n}$ as required by the promotional model[9]; therefore, f emission from $R^{2+}c^{n}$ yields a single spectral feature at E_F. This picture breaks down in Ce-based systems, where the photoemission spectra reveal two spectral features, one which is typically several electron volts from E_F, and one which is near E_F.[11] A systematic study of the photoemission in γ-cerium has established the $4f$ character of both spectral features.[12]

The nature of the $4f$ state in cerium-based systems, whether the Ce atoms are "mixed valent" (i.e., far from a stable trivalent description) or can be described as forming a Kondo lattice (close to a stable trivalent description) is often difficult to decide.[13] For instance, it is not clear at this point whether the bimodal structure seen clearly in the valence-band photoemission is γ-cerium (which is weakly mixed valent) is a reflection of the ground state or a result of the photoemission process. Despite this interpretational problem, it is clear from previous studies that valence-band photoemission, particularly if done with variable photon energy as obtained with synchrotron radiation, provides, apart from a view of the valence band, an unmistakable view of the $4f$-derived features. The photoemission study reported herein was undertaken to illuminate differences in the $4f$ character and/or band structures in the Kondo-lattice systems CeT_2Si_2 (with T=Cu, Ag, Au, or Pd). It was hoped that the results of this study might also bring us a step closer to understanding the origin of the bimodal spectrum seen clearly in Ce-based systems which are far from the stable $4f$ description.

II. EXPERIMENTAL DETAILS

Samples of $CeCu_2Si_2$, $CeAg_2Si_2$, $CeAu_2Si_2$, and $CePd_2Si_2$ were prepared by arc-melting the pure materials on a water-cooled copper hearth in an argon atmosphere. All of the starting materials were nominally $>99.9\%$ pure or better with respect to metals. The raw materials were melted together and the resulting boule was flipped over and remelted six to eight times. Each sample was then wrapped in tantalum foil, sealed in an evacuated quartz tube, and annealed for four to five days at 800 °C. X-ray diffraction confirmed that the samples were single phase (to within the resolution of the technique, $\sim 5\%$) with the $ThCr_2Si_2$ structure. From the boules prepared as above and for use in the photoemission experiments, samples were extracted and shaped into parallelepipeds with approximate dimensions of $4\times4\times6$ mm.

The photoemission studies were made with the IBM display-type analyzer[14] using synchrotron radiation at the Synchrotron Radiation Center of the University of Wisconsin—Madison. This system was operated in an angle-integrated mode with a total (electrons and photons) energy resolution of ~ 0.15 eV at $h\nu=70$ eV. The sample was first introduced into a preparation chamber (vacuum $\sim 2\times10^{-10}$ Torr), where a fresh surface was exposed by fracturing the sample. Following this, the sample was immediately transferred to the measuring position, where the vacuum was better than 10^{-10} Torr. The surface cleanliness, with respect to all important contaminants, was confirmed by Auger spectroscopy and photoemission at low $h\nu$ to check for hydrogen contamination. In addition, the Si $2p$ core level was a very sensitive monitor of the surface cleanliness.

III. EXPERIMENTAL RESULTS

A broad view of the photoemission spectra at $h\nu=70$ eV for CeT_2Si_2 (T=Cu, Ag, Au, and Pd) and for the Pd reference system $LaPd_2Si_2$ is shown in Fig. 1. The intensities of the spectra have been normalized by scaling them according to the peak height of the dominant feature. A visual inspection of the spectra suggests that the alternate procedure of normalizing according to the integrated intensity, i.e., from 0 to 10 eV, would produce similar results. At this photon energy, the spectra are dominated by the T-derived d bands. The general signatures of the dominant spectral features are recognized as d-band emissions by comparing the spectra to those obtained for the corresponding elemental T metals (Cu, Ag, Au, and Pd; see, e.g., Refs. 15 and 16). The d-emission features are shifted, relative to the pure T metals,[15,16] by roughly 2 eV to higher binding energies. The cross-hatched regions highlight the spectral region near E_F (0—1 eV), which is expected to mimic the density of states near E_F (if proper account is taken of the relative photoemission cross sections of s, p, and d electrons). The emission in this region is predominantly of T-derived d character, since the s and p electrons have a much smaller photoemission cross section at $h\nu=70$ eV than the d electrons and cannot explain the differences in the intensities at E_F between the spectra.[17] By studying the $h\nu$ dependence of this part of the spectrum, we can also conclude that these differences are not due to the Ce 5d electrons.[18] We have previously studied the $h\nu$ dependence of the d-band emission in $La_{0.9}Th_{0.1}$, $Ce_{0.9}Th_{0.1}$, and $Pr_{0.9}Th_{0.1}$.[12] Now, we

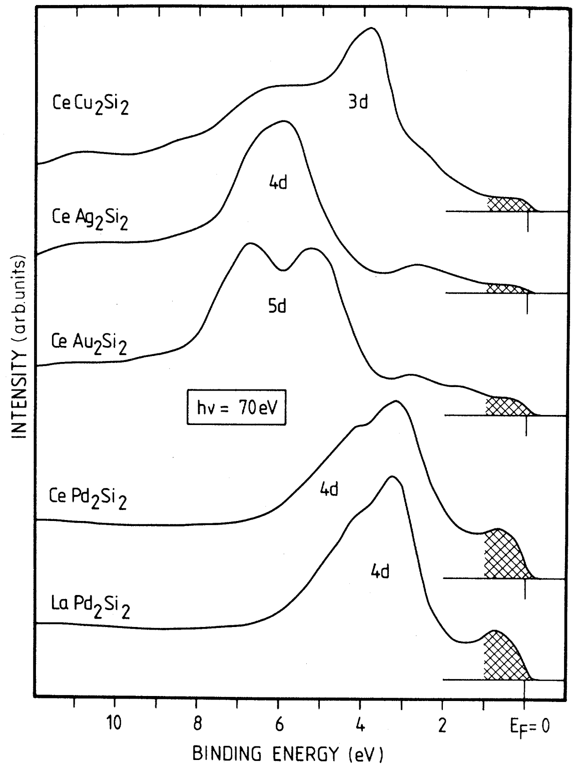

FIG. 1. Photoemission energy-distribution curves (EDC's) at $h\nu=70$ eV for CeT_2Si$_2$ ($T=$Cu, Ag, Au, and Pd) and LaPd$_2$Si$_2$ at room temperature. The curves are normalized to maximum emission intensity. The cross-hatched area (0—1 eV) increases in following the sequence Ag, Cu, Au, Pd (see text).

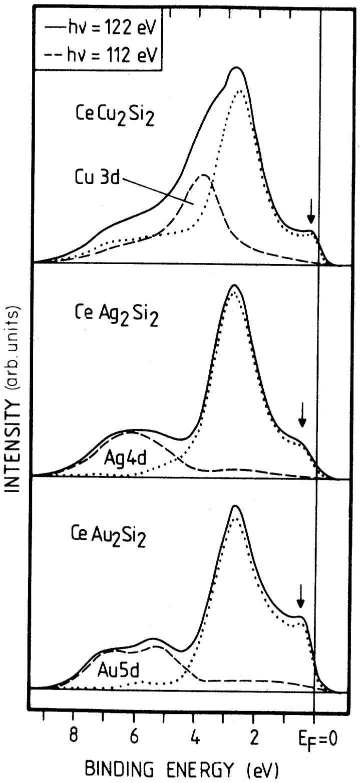

FIG. 2. EDC's for CeCu$_2$Si$_2$, CeAg$_2$Si$_2$, and CeAu$_2$Si$_2$ taken on resonance ($h\nu=122$ eV, solid line) and off resonance ($h\nu=112$ eV, dashed line) after normalization to equal intensities for binding energies $\gtrsim 8$ eV and background subtraction. The difference curve (dotted line) represents the $4f$ contribution. The arrows indicate the positions of the maximum of the emission feature near E_F.

find for the systems presently studied that the T-derived d intensity (taken from the main peak in the spectra) decreases approximately 10 times less as we go from $h\nu=30$ to 70 eV than the RE $5d$ emission. However, in the RT_2Si$_2$ systems, the emission close to E_F shows about the same $h\nu$ dependence as the main T-derived d bands. This implies that both these features must be dominated by the T-derived d-band emission, and especially that the Ce $5d$ contribution to the 70-eV spectra must be very small. Furthermore, since *all* parts of the RT_2Si$_2$ spectra in Fig. 1 are dominated by the T-atom d-band emission, the normalized (to the total area of the spectrum) intensity at E_F provides an approximate measure of the partial-T density of states in this region. The Pd-based systems exhibit considerably larger spectral intensity near E_F because of the closeness of the Pd $4d$ band to E_F. At $h\nu=122$ eV, there is a giant resonance in the Ce $4f$ emission, which was first observed by Johansson *et al.*[19]; hence, a particularly clear view of the Ce $4f$ spectrum can be obtained by utilizing this photon energy, as seen in Figs. 2 and 3. The resonance in the Ce $4f$ emission has been identified as resulting from the transition $4d^{10}4f^1 \rightarrow 4d^9 4f^2$, followed by the Auger decay process $4d^9 4f^2 \rightarrow 4d^{10}4f^0 + e^-$, the latter process being a so called "super-Coster-Kronig" transition.[20] The dominance of the Ce $4f$ emission becomes particularly pronounced for the Ag, Pd, and Au compounds due to the closeness of the energy of the (broad) Cooper minima for the $4d$ and $5d$ emissions.[21] Also shown in Fig. 2 are the spectra recorded at 112 eV, which is an antiresonance for the $4f$ emission (see, e.g., Ref. 22). The 122 and 112 eV spectra are normalized so as to give similar intensities in the energy range above the $4f$ emission ($\gtrsim 4$ eV). The 112 eV spectra exhibit emission features which originate from the T metal and Si valence electrons. For all of the compounds except CeCu$_2$Si$_2$, there is practically zero intensity in the region of the Ce states (0—3 eV). In the case of Cu, the more intense $3d$ band interferes with the deeper

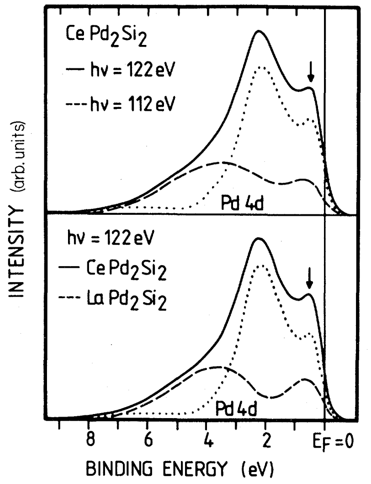

FIG. 3. Illustration of different subtraction procedures for $CePd_2Si_2$. Upper panel: On-resonance ($h\nu = 122$ eV, solid line) and off-resonance ($h\nu = 112$ eV, dashed line) curves produce a difference curve (dotted line) as in Fig. 2. Lower panel: At constant photon energy $h\nu = 122$ eV, $CePd_2Si_2$ (solid line) and $LaPd_2Si_2$ (dashed line) result in a similar difference spectrum (dotted line) as in the upper panel, indicating negligible variation of the Pd emission for $h\nu = 122$ and 112 eV. The arrows indicate the positions of the maximum of the emission feature near E_F.

part of the Ce $4f$ structure. The T- and Si-derived photoemission intensities vary rather slowly with the photon energy, thus also at 122 eV, these contributions are very small (except for the Cu compound in the deeper part of the spectrum).

The peak in the major Ce$4f$ emission occurs at energies ranging from ~ 2.2 eV for $CePd_2Si_2$ to ~ 2.6 eV for $CeAg_2Si_2$ for the four systems shown in Figs. 2 and 3. We point out that the location of the f-emission peak is not necessarily the location of the $4f$ level in the ground state as is often suggested or claimed in the literature, but rather, and explicitly, it is the energy required to create a localized, screened $4f$ hole. As discussed in Sec. I, an additional feature near E_F has been previously observed in the valence-band photoemission spectra of Ce-based systems and its f character has been confirmed in the case of γ-cerium.[12] This feature is also clearly present in Figs. 2 and 3 in the spectra recorded at 122 eV. In an attempt to isolate it, we have constructed difference spectra in Figs. 2 and 3. The feature near E_F in the Ce-based systems is clearly resolved in the $(122-112)$-eV spectra. Note that the appearance of the peak at E_F is not a result of the subtraction procedure, but it is clearly already seen in the 122-eV spectra. An alternate subtraction procedure is exhibited for $CePd_2Si_2$ in Fig. 3, namely, the subtraction of the spectrum for $LaPd_2Si_2$ recorded at the same photon energy (122 eV). Again the feature near E_F persists. In order to further concentrate on this feature, in Fig. 4 we have collected all four difference spectra normalized to the total integrated electron-distribution curve (EDC) intensity. This allows a comparison of the intensities of the features near E_F for the different Ce-based systems. It is seen that the intensity of the feature appears to roughly track the intensity of the T-derived d density of states near E_F, the latter depicted by the cross-hatched regions of the 70-eV spectra in Fig. 1. Thus, a comparison of the intensities with the d projection of the density of states near E_F reveals that one has to be cautious before assigning f character to it, for, even in the original work on cerium,[19] it was found that, although f emission is particularly enhanced at the 122-eV resonance, (d-dominated) band emission near E_F was also enhanced at the resonance. This reflects the presence of the auxiliary decay channel $4d^9 4f^2 c^n \rightarrow 4d^{10} 4f^1 c^{n-1} + e^-$, where c represents a conduction-band electron (assumedly of strong d character in the present case) and the final state is a band hole instead of a $4f$ hole. Therefore, we have to consider the possibility that with either subtraction procedure exhibited in Fig. 3, i.e., $122-112$ eV or Ce(122 eV)$-$La(122 eV), the remaining emission near E_F could be dominated by the above resonant band-emission channel. In the case of γ-cerium, it was possible to establish the f

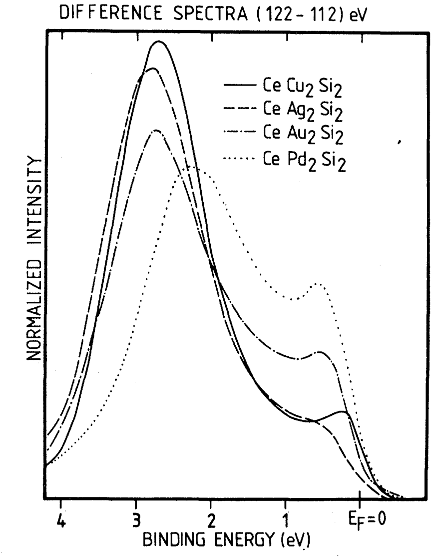

FIG. 4. Difference spectra from Figs. 2 and 3, upper panel, normalized to the total integrated intensity. Note the variation of the emission intensity of the features near E_F and the different peak positions for $CeCu_2Si_2$ and CeT_2Si_2 (T = Ag, Au, and Pd).

character of the feature observed near E_F not from the spectra recorded in the region of the giant f-emission resonance but rather by comparing the spectra for γ-cerium, lanthanum, and praseodymium in the photon-energy range 30—70 eV.[12] In the present case, a similar procedure is not possible because the spectra at the lower photon energies (e.g., 30—70 eV) are dominated by T-derived d emission. Instead, we shall discuss the Ce(122 eV)—La(122 eV) subtraction in more detail. The photoabsorption curve for Ce in the vicinity of the $4d$ ionization threshold shows a region of fine structure (100—115 eV), followed by a giant resonance which has its maximum at $h\nu = 122$ eV.[23] Lanthanum has a corresponding giant resonance, but the maximum absorption is already reached at 118 eV.[23] However, these resonance structures are broad and at $h\nu = 122$ eV, the La absorption is still close to its maximum. We expect the La $5d$ conduction-band photoemission to track the $5d$ photoabsorption curve in the same way as the Ce band emission. If the resonating peak closest to E_F in $CePd_2Si_2$ were due to the Ce $5d$ conduction-band electrons, we would expect a corresponding peak to appear in the spectrum of $LaPd_2Si_2$ at the La resonance (as well as at $h\nu = 122$ eV). As seen from the comparison in Fig. 3, this is not the case. Therefore, we conclude that the peak at E_F in the 122-eV spectrum of $CePd_2Si_2$ is $4f$ derived. The low La intensity in Fig. 3 suggests that all the (122—112)-eV difference spectra of Figs. 2 and 3 show the $4f$ states almost entirely, and, to a much lesser extent, the $5d$ levels. A similar comparison between U and Th systems was presented in Ref. 24 and showed analogous results.

IV. DISCUSSION

While we could not definitely establish the f character of the anomalous feature near E_F in the present study, it was possible to correlate the intensity of the feature with the T-derived d density of states near E_F. To the extent that the feature near E_F has f character, as it has been established to have in cerium[11,12] and $CeAl_2$,[25] we can argue that a large d density of states near E_F might have the effect of altering the spatial distribution of the $4f$ state so as to increase the (negative) f-d hybridization energy. As evident from a comparison of the EDC's for $CeCu_2Si_2$ and CeT_2Si_2 ($T =$Ag, Au, and Pd) in Figs. 2 and 3, the positions of the peak maxima (indicated by arrows) near E_F are different. In Fig. 4, this observation is even more obvious, and we read 0.25 eV for the maximum in superconducting $CeCu_2Si_2$, while we find it at significantly higher binding energies (~ 0.6 eV) in the three magnetic systems. This could point to a markedly higher density of f states within the millivolt vicinity of E_F in $CeCu_2Si_2$ than in the other systems. That we do not get a clearer view is partly due to the limited experimental resolution ($\gtrsim 150$ meV) and (probably more important) intrinsic relaxation processes of photoemission itself.[11,12] Accordingly, we expect significantly smaller electronic specific-heat values (yet to be measured) for CeT_2Si_2 ($T =$Ag, Au, and Pd) than the $\gamma \simeq 1\ \mathrm{J\,mole^{-1}\,K^{-2}}$ value attributed[4] to heavy fermions in $CeCu_2Si_2$.

The present results, together with previous studies of the magnetic susceptibility and resistivity,[4,6] suggest that the Ce $4f$ moment in $CePd_2Si_2$ is unstable as it is in $CeCu_2Si_2$, yet $CePd_2Si_2$ orders antiferromagnetically at ~ 10 K, whereas magnetic ordering in $CeCu_2Si_2$ is inhibited down to ~ 0.5 K, where the system becomes superconducting. Further evidence for the instability of the $4f$ state in $CePd_2Si_2$ is provided by recent neutron-diffraction measurements[26] on the antiferromagnetic state. The Ce moments are found to be appreciably reduced from their stable values, if one assumes that the crystal-field ground state for $CePd_2Si_2$ is the same as that identified for $CeCu_2Si_2$.[27] On the other hand, neutron-diffraction studies[26] of the antiferromagnetic state in $CeAu_2Si_2$ reveal fully developed Ce moments. We hypothesize that the relative strengths of the moment fluctuations and the magnetic exchange, hence, the ground-state behavior, may depend upon the relative strengths of the T-derived and RE-derived density of states at E_F. Angle-resolved valence-band photoemission on this class of materials (in single-crystalline form) in conjunction with band-structure calculations[28] will prove very useful in illuminating band-structure details which appear to be highly sensitive to the transition-element component.

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