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Temperature-Invariant Photoelectron Spectra in Cerium Heavy-Fermion Compounds: Inconsistencies with the Kondo Model

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$4f$ levels in Ce heavy-fermion compounds are examined using resonant photoemission. We find the following inconsistencies with the predictions of the Kondo model: (a) All temperature dependence can be accounted for simply by phonon broadening and the Fermi function; (b) the spectral weights of the features near E_F do not scale with T_K; and (c) the line shape of the feature previously identified as the Kondo resonance is Lorentzian and about an order of magnitude broader than predictions. Instrument resolution is not a limiting factor.

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A number of theories [1,2] have been employed to explain the unique electronic properties of heavy-fermion materials. Models [3,4] based on the single-impurity Anderson Hamiltonian predict an intense many-body or Kondo resonance (KR) near E_F having f-electron character. Within the formalism of the Kondo model (KM), the valence-band density of states (DOS) is dominated by two regions [1]; the first region is at ≈ -2 eV below the Fermi level (E_F) representing the $4f^1 \rightarrow 4f^0 + e^-$ transition, and the second region is generally within ± 0.3 eV of E_F and encompasses the KR and any spin-orbit or crystal-field sidebands. Division of the $4f$ occupancy weight between the two regions is determined by the ambient temperature (T) and Kondo temperature (T_K). Central to the concept of the KM is the KR at an energy $\approx k_B T_K$ above E_F, having a width $\approx k_B T_K$ and a weight at $T=0$ K of $\approx \pi T_K/\Gamma$, where Γ is the hybridization width between the $4f$ levels and the valence band [4]. Clearly, large variations in the spectral weight of the KM-related features are expected [4] with T_K. In the extreme case of $T_K=0$ one expects no $4f$ features near E_F. In addition to the main KR, there may exist Kondo-related features attributed to spin-orbit (SO) and crystal-field (CF) effects [3,4]. These features have characteristic temperatures T_{KSO} and T_{KCF}, respectively, and are expected to have occupancy below E_F. T_{KSO} and T_{KCF} depend inversely on the degeneracy N of the appropriate $4f$ level and thus may be as large [4] as $(5\text{–}10)T_K$. The qualitative behavior with temperature, however, remains the same. For example, varying the temperature from $T=0$ K to $T=T_K$ (T_{KSO} or T_{KCF} for sidebands) the amplitude should decrease by a factor of 3, and for $T=5T_K$ a factor-of-10 decrease is expected. The total weight appears to be conserved with T in some models [3] but less clearly so in others [4,5].

We have used high-resolution synchrotron radiation photoelectron spectroscopy at the Ce $4f$ resonance energy (120 eV) to experimentally determine the $4f$ character in several Ce-based compounds and compared the results with KM predictions [4]. A detailed temperature study was done for previously reported [6] $CeSi_2$, for which $T_K \approx 35$ K (≈ 3 meV) with the Ce $4f$ $J=\frac{5}{2} \rightarrow \frac{7}{2}$ spin-orbit splitting $\Delta_{\mathrm{SO}} \approx 280$ meV and the crystal-field splitting $\Delta_{\mathrm{CF}} \approx 35$ meV. For these parameters the KM predicts photoemission spectra containing three features identified as (i) the $4f^0$ final state at ≈ -2 eV, (ii) the $4f_{7/2}$ SO final state at ≈ -280 meV, and (iii) the CF final state at ≈ -35 meV. The actual KR for $CeSi_2$ is predicted to be just above E_F. Thus the temperature scales that enter into the $CeSi_2$ problem are T_{KCF} and T_{KSO}. The T_K's for the other systems reported in this work are as follows [7]: $T_K \approx 3$ K for $CeAl_3$, 300 K for $CeBe_{13}$, while ferromagnetic $CeSb_2$ ($T_C \approx 10$ K) gives no indication of Kondo-like behavior [8] in the bulk properties, and thus $T_K \approx 0$. The previous $CeSi_2$ work of Patthey and co-workers [6] is the highest-resolution photoemission data on any heavy-fermion system to date. As such, we will draw on the valuable experimental results of this previous work and compare it with our own data, the Kondo model, and a vastly simpler explanation of the temperature dependence consisting of nothing more than phonon broadening and the Fermi function.

We state at the outset that the systematics observed in bulk property measurements [7] support the concept of a KR and we do not question the thermodynamic interpretations. Rather we ask here, can the observed photoelectron spectra (PES) features be identified as such? Indeed, we will show that the present body of experimental results does not justify identification of photoemission features at E_F as the predicted KR or its sidebands.

Experiments were carried out at the Los Alamos U3C beam line at the National Synchrotron Light Source and the University of Wisconsin's Synchrotron Radiation Center. The total experimental resolution was determined to be 95 meV for high resolution and 180 meV for medium resolution. The temperature was controlled by placing the sample in direct contact with a cryostat cooled by either liquid helium ($T \approx 15$ K) or liquid nitrogen ($T \approx 80$ K), or held at room temperature ($T \approx 300$ K), and the chamber base pressure was $\approx 5 \times 10^{-11}$ Torr. Further details will be documented in a forthcoming publication [9].

Results for $CeSi_2$ are presented in Fig. 1 along with two fits to the data for the near-E_F region. The data are represented by dots and the fits by lines. The single spectrum from Patthey and co-workers [6] is presented in the topmost and again in the third spectrum of the figure, and consists of difference curves from He I ($h\nu=21.2$ eV)

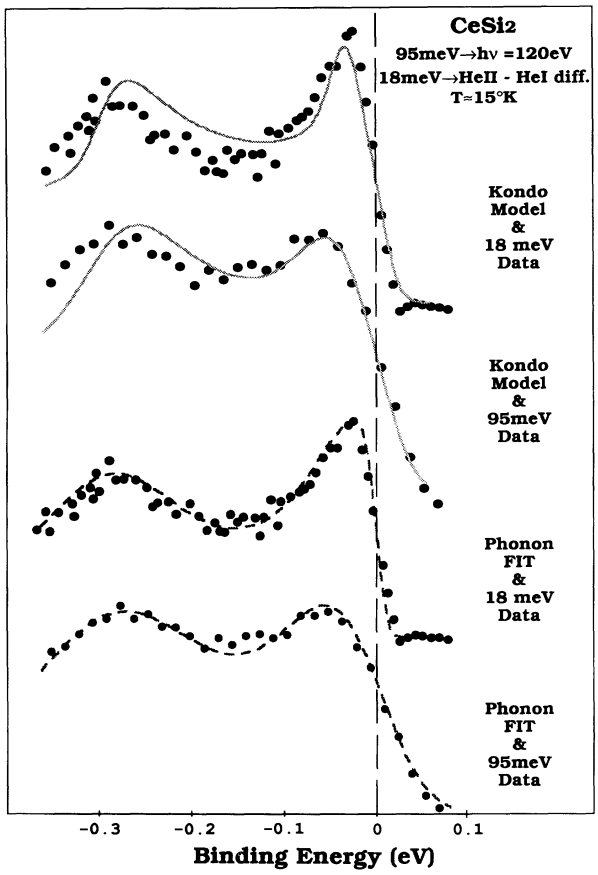

FIG. 1. Photoelectron spectra for $CeSi_2$ in the near-E_F region. The 18-meV data are from Ref. [6], taken with $h\nu=40.8$ eV, while the present work are 95-meV data with $h\nu=120$ eV, $T\approx 15$ K. The Kondo-model fit is from Ref. [6], while the phonon fit is the present work. See text for details.

and HeII ($h\nu=40.8$ eV) data to extract the f character. The resolution for the He lamp data is 18 meV [6]. Our resonance ($h\nu=120$ eV) spectrum is shown in the second and again in the bottommost data of the figure with a resolution of 95 meV. The 18- and 95-meV data show the same two prominent features with the peak-to-valley ratio appropriately larger in the 18-meV data. The temperature was ≈ 15 K for both sets of data allowing for minimum phonon and Fermi-function broadening while providing a suitably low temperature to observe any predicted Kondo resonance.

The fit to the topmost spectrum of Fig. 1 is from Ref. [6] using the KM, with parameters appropriately varied to obtain best fits for $CeSi_2$. The fit to the second spectrum of the figure is the same as the topmost fit but now with 95-meV broadening to account for the different experimental resolution. A superficial glance might indicate an acceptable fit, but careful examination reveals important discrepancies in energy position and especially in width.

The same two data sets are much better fitted with simple Lorentzian line shapes in the third and bottommost spectra of Fig. 1. The specifics of the fitting are as follows: Two Lorentzians are centered at -20 and -280 meV, with FWHM of 145 and 220 meV, respectively, Gaussian broadened by 18 and 95 meV for the data of Ref. [6] and this work, respectively, and cut off by an ≈ 15 K Fermi function. The only difference between these latter two fits is the Gaussian width which is fixed at the value of the stated experimental resolution. We can see that whatever the nature of the feature at E_F, *its natural linewidth is 145 meV*, an order of magnitude larger than expected from the KM. One benefit of this experimental finding is that our 95-meV resolution is not limiting our experiment, since our data are entirely consistent with that of Ref. [6]. If the Kondo resonance is as narrow as predicted, the observed line shape would be characteristic of the resolution and have a width comparable to the measured resolution (18 meV for Ref. [6] and 95 meV for our data). This is *not* the case for the heavy-fermion systems presented in our paper or in Ref. [6].

Aside from the width, a second crucial test of the KM is the temperature dependence of the resonance. Patthey and co-workers [6] have reported such a temperature dependence for the near-E_F peak in $CeSi_2$ and concluded that the use of the strong-coupling many-body KM theory [3,4] is justified. However, since every material displays some temperature dependence, the KM effects must be *over and above* the ordinary effects of the Fermi function and phonon broadening. We determined the phonon broadening from a fit of the Si $2p$ core levels (see Ref. [10] for details) at various temperatures and applied this same broadening to the valence-band features. Using a photon energy of 120 eV, we were able to measure the valence band and the Si $2p$ core level at the same photon energy and resolution. The inset of Fig. 2 shows a typical fit quality. Use of the Si $2p$ phonon broadening for the Ce $4f$ levels is justified since both features have very small radial wave-function distributions compared to the interatomic spacing for $CeSi_2$, and will be similarly affected by lattice vibrations [11]. The results of these measurements are presented in Fig. 2. The fitting of the features at E_F was carried out as follows: The Lorentzian positions, widths (FWHM), and relative intensities are obtained from the Lorentzian fits of Fig. 1, and are fixed for all three temperatures. The variables are the temperature (determined by a thermocouple) used in the Fermi function, and the Gaussian broadening extracted from the Si $2p$ data (these are not *adjustable* parameters). In the low-temperature case ($T\approx 15$ K), the Gaussian broadening represents the instrument response functions only, but at elevated temperatures the finite phonon broadening, up to 88 meV at 300 K, is included through a root-mean-square dependence. The fits at all three temperatures ranging from near liquid helium to room temperature are very good, thus leaving no room for any additional temperature effects from the KM.

A study of valence-band properties for Ce-based com-

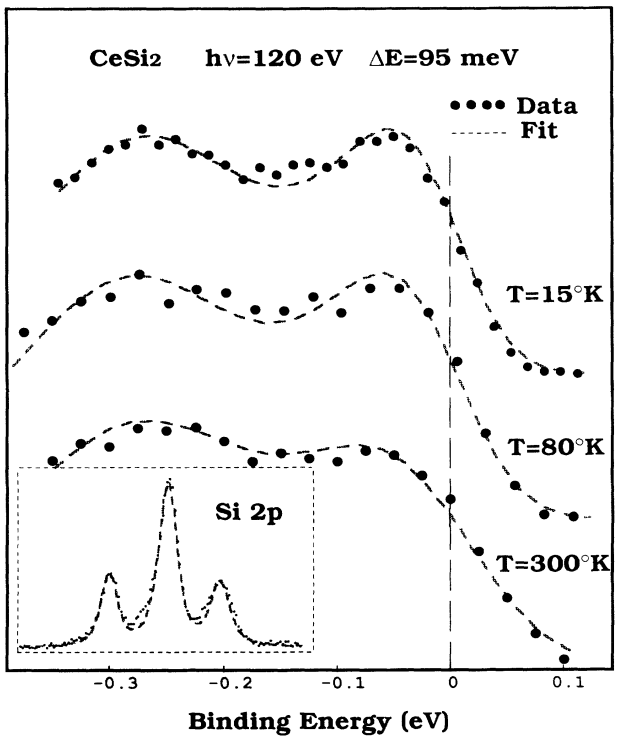

FIG. 2. Fits at various temperatures to the $CeSi_2$ spectra in the near-E_F region. All fitting parameters are the same in the three spectra except for the Fermi function and phonon broadening. The topmost spectrum and fit (at a temperature of ≈ 15 K) is the same as the bottommost spectrum in Fig. 1. The phonon broadening for the other temperatures was obtained from a fit to the Si $2p$ core levels (typical fit shown in the inset).

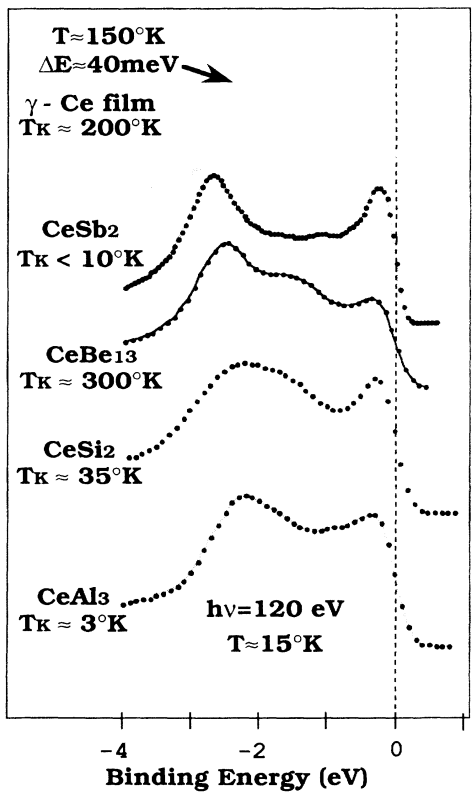

FIG. 3. Low-resolution ($\Delta E \approx 180$ meV) valence-band spectra for several materials at ≈ 15 K taken at resonance (γ-Ce is from Ref. [12] at $\Delta E = 40$ meV). There is no apparent systematics with thermodynamically derived T_K's.

pounds with a wide range of T_K's is presented in Fig. 3 to check for systematics of the spectral weights of the presumed KM-related features with T_K. (The spectrum for γ-Ce, $T_K \approx 200$ K, is from Ref. [12].) For $CeAl_3$, $CeSi_2$, and $CeBe_{13}$, T_K varies by 2 orders of magnitude (3–300 K), while $CeSb_2$ bulk properties [8] show no Kondo behavior (i.e., $T_K \approx 0$). Except for γ-Ce, Fig. 3 represents moderate-resolution, long-range scans at temperatures of ≈ 15 K. Recall that the weighting of the KR and the sideband region, with respect to the "−2-eV" region, depends [3] directly on T_K (or T_{KSO}, T_{KCF} as the case may be), yet we see no variation in the near-Fermi-level emission which correlates with T_K's determined from thermodynamic or neutron data. This contrasts sharply with Fig. 18 of Ref. [6], where a different set of compounds yielded some semblance of systematics (with T_K's determined self-consistently). Most notably, in Fig. 3, $CeSb_2$ shows strong emission in the 0 to −0.3 eV regime which is reserved in the KM for the many-body resonances, presumed negligible in this compound.

Finally, high-resolution spectra of the near-E_F region are shown in Fig. 4 to again check for any systematics with T_K. The $CeSi_2$ spectrum is the same as in Fig. 1, while γ-Ce is again from Ref. [12]. With the addition of $CeAl_3$, $CeSb_2$, and $CeBe_{13}$, a trend becomes obvious: *The near-E_F region is generally characterized by two temperature-invariant features, independent of T_K.* The assignment of these two features to a Kondo resonance or SO and CF sidebands is questionable, since these five materials have widely varied crystal structures [6] and T_K's which should affect both the CF splittings and the spectral weights. More importantly, $CeSb_2$ prominently shows these same two features where one would expect them to be minimal. The observation that these emission features are independent of T and T_K is easier to understand via models where different features arise from different final-state screening channels [2,13] for the Ce $4f$ level. If the Kondo resonance still exists on top of this electronic structure [2,14], it must have much less spectral weight than reported in previous PES studies.

In conclusion, we have shown that high-resolution photoemission results of $CeSi_2$ and other heavy-fermion compounds are not consistent with a KM description. To wit, (i) the temperature dependence requires no explanations beyond that of simple phonon broadening and the Fermi function; (ii) the natural linewidth of the feature usually identified as KR related is much too large; (iii) the spectral weights and line shapes show no obvious systematics with T_K. Indeed, Ce $4f$ emission at −2 eV, as well as the

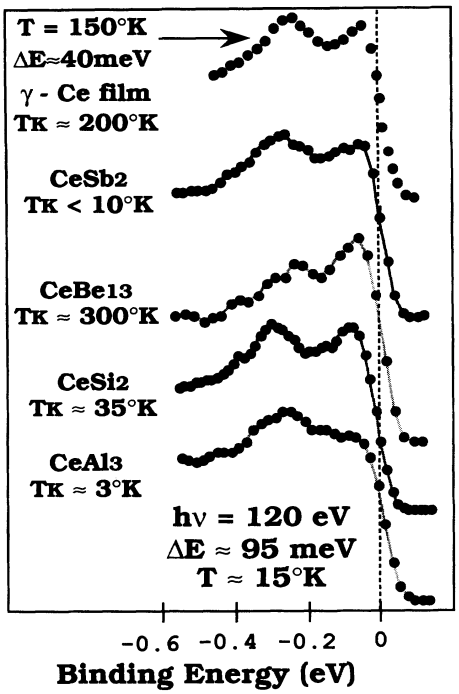

FIG. 4. High-resolution (ΔE =95 meV) spectra in the near-E_F region for the compounds of Fig. 3. Note that the double-peaked structure is a general feature of Ce $4f$ emission unrelated to T_K and crystal structure.

double feature in the near-E_F region, appears to be a general characteristic of Ce, suggesting that it may arise from different final-state screening channels [2]. Our observations do not disprove the existence of a many-body resonance; they do, however, show that the interpretation of the observed spectra in terms of these resonances is likely in error, and points to a need for a reexamination of the assumed ground state.

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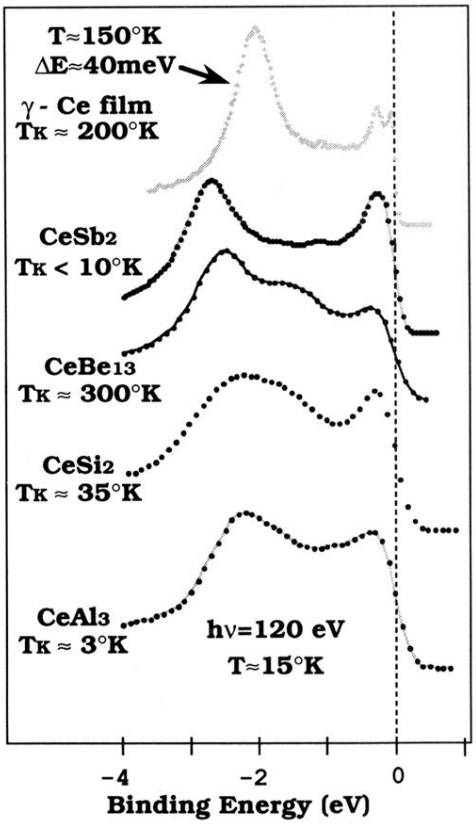

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