# High-Temperature Collapse of the Kondo Resonance in $CeSi_2$ Observed by Photoemission

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(Received 2 February 1987)

uv-photoemission spectra of $CeSi_2$ have been measured with a resolution of 18 meV in the temperature range $15\ \mathrm{K} < T \leq 300\ \mathrm{K}$. The spectral analysis has been performed within the Anderson single-impurity model using the noncrossing approximation and including $4f$-spin-orbit and crystal-field splittings. It accounts perfectly for the observed flattening of the fine structures in the spectra when the temperature increases. This study confirms indisputably the many-body nature of the low-lying excitations around $E_F$ observed with photoemission.

PACS numbers: 79.60.Cn, 71.70.Ms, 72.15.Qm, 76.30.Kg

The low-energy electronic excitations within $k_BT$ play an essential role in the transport properties, the magnetic susceptibility, and the electronic specific heat of condensed matter. For normal metals the correlation between the conduction electrons does not lead to dramatic deviations from the nearly free-electron model down to the lowest temperatures. In highly correlated electronic systems, however, an important enhancement of the low-temperature specific heat is observed which can be formally accounted for by renormalizing the electron mass in the free-electron–model formulas. Recently, a new class of metals containing elements at the beginning of the $4f$ and $5f$ series has been discovered which exhibit a variety of extremely anomalous low-temperature properties.[1] For example, the linear coefficient of the specific heat $\gamma$ $(T \rightarrow 0)$ reaches magnitudes of the order of 1 J/mole $\mathrm{K}^2$, which would correspond to an effective electron-mass enhancement of a factor of 1000 in the free-electron model. Hence, the term heavy-electron metal[2,3] has been coined to characterize these systems. A possibility to visualize an extremely high specific heat in a single-particle approach is to consider that it can be attributed to the fraction of the thermally excited electrons in a band of width $k_BT_0$, $C(T) \sim nk_B(T/T_0)$.[4] In heavy-electron systems this approach yields bandwidths of the order of 1 meV, which is typically $10^{-3}$ of the Fermi energy in usual metals. A simple single-particle origin of such a high and narrow density of low-energy excitations appears, however, not to be tenable. The essential arguments against this description are (i) that the ground state would clearly favor ferromagnetism and (ii) that the number of electrons forming such peaks is not sufficient to account for the large entropy observed at $T > T_0$.[4]

It is now generally accepted that the weak hybridization between the extended electron states and the highly correlated $f$-electron states is the key mechanism that gives rise to the many-body nature of the heavy-electron manifestations.[5] For dilute Ce systems, the Anderson single-impurity model, containing this hybridization as an essential ingredient, predicts[6,7] that with decreasing temperature a resonant structure ("Kondo resonance") develops within an energy $k_BT_0 = \delta$ above $E_F$, which sets a new energy scale to all low-temperature properties. The impurity model is obviously not adapted to account for any coherence effect between the different $f$ sites in a lattice.[4] However, it has appeared to be very successful in the interpretation of high-energy spectroscopic data,[5] and recently, the low-lying excitations within $\delta$ have been directly observed with high-resolution (20 meV) photoemission in Ce metal[8] and CeN.[9] The aim of the present Letter is to investigate the temperature-dependent development of the Kondo resonance in order to obtain a conclusive test of the many-body concepts invoked to explain the unconventional temperature dependence of the properties of heavy-electron systems.

As a suitable candidate for this investigation, the compound $CeSi_2$ was chosen. It crystallizes in the tetragonal $\alpha$-$ThSi_2$ structure, where each Ce atom is bonded to twelve silicon atoms at an interatomic distance of 3.13 Å.[10] The magnetic susceptibility shows a breakdown of the Curie-Weiss law at low temperatures without any indication of ordering.[11,12] Heat-capacity measurements exclude magnetic ordering or crystal-field transitions below 70 K down to 0.1 K and yield a linear coefficient of the specific heat $\gamma(T \rightarrow 0) \approx 100\ \mathrm{mJ/K^2\ mole}$.[11,12] These facts point to $4f$-spin compensation by the conduction electrons at low temperature and consequently $CeSi_2$ has been considered as a dense Kondo system.[13] $\gamma(T \rightarrow 0)$ is already strongly enhanced when compared to normal metals, but is still 1 order of magnitude smaller than in extreme heavy-electron compounds[14,15] such as $CeCu_6$ in which the photoemission Kondo peak of weight $n_f(1-n_f)$ ($n_f$ is the $f$ population per Cu atom)

and width $\delta$ is too weak to be detected with the best resolution achieved presently.[16] From the relationship[17] $\gamma \sim 1/\delta$ it appears immediately that $CeSi_2$ can be expected to offer a favorable situation for studying the behavior of the Kondo peak.

The polycrystalline sample of $CeSi_2$ was prepared by melting stoichiometric amounts of Ce and Si in a levitation furnace. Homogenization was achieved by repeated melting and subsequent tempering at 1100 K for 2 days. Analysis of the Debye-Scherrer patterns showed that only a single phase with the $\alpha$-$ThSi_2$ structure was present.[18] The photoemission measurements were performed in a spectrometer equipped with a commercial gas-discharge lamp producing the very narrow photon lines of 21.2 eV (He I) and 40.8 eV (He II).[8] The sample was cooled at about 15 K with a closed-cycle He refrigerator. Elevated temperatures up to 300 K were obtained by the heating of the cold finger during refrigeration. During the measurements the vacuum was $3\times10^{-10}$ Torr and the oxygen and carbon contamination of the surface was maintained below the detection limit by frequently scraping *in situ* with an $Al_2O_3$ file. The spectra were taken with a total resolution of 40 meV [Fig. 1(a)] and 18 meV [Figs. 1(c)–1(f)].

Figure 1(a) shows, between 4 eV and $E_F=0$ eV, the photoemission spectra of $CeSi_2$ excited with the two photon energies at the lowest sample temperature (15 K) which could be obtained. For $h\nu=21.2$ eV the spectrum contains essentially a broad structure around 2 eV which, by comparison with x-ray photoemission spectra,[19] must be partly attributed to emission from Si states of $3p$ character. When the photon energy is raised to 40.8 eV, the $4f/3p$ cross section increases by a factor[20] of 6 and, in addition to the strengthening of the broad 2-eV peak, two sharp structures emerge near the Fermi energy, which can only be barely discerned at 21.2 eV. This cross-section dependence clearly reveals the $f$ character of the three emission features. The emission intensity from states of other symmetries is estimated to be roughly given by the dashed line in Fig. 1(a). Our spectra are consistent with previous resonant photoemission data[21] which were recorded at room temperature with a resolution roughly a factor of 10 poorer and consequently could not resolve the interesting peaks close to $E_F$. By comparison of the present results with those of Ce metal,[8] the structures around 2 and 0.3 eV are identified with final states of mainly $4f^0$ and $4f^1_{7/2}$ character, respectively. The peak at $E_F$ originates from the low-lying excitations closely related to the ground state.

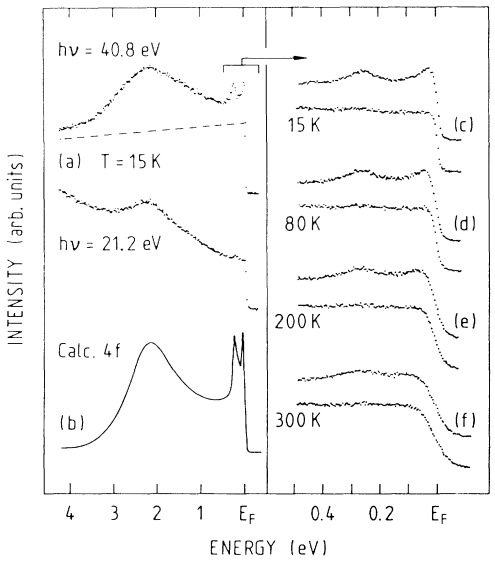


FIG. 1. (a) Photoemission spectra of $CeSi_2$ measured at $T=15$ K with a resolution of 40 meV. The dashed line indicates the emission intensity from non-$f$-symmetry states. (b) Simulation of the $f$ contribution by a many-body calculation for finite temperature including $4f$ spin-orbit and crystal-field splittings. The curve has been convoluted with a Gaussian of 40 meV FWHM in order to account for the instrumental resolution. (c)–(f) Photoemission spectra of $CeSi_2$ (upper curves, He II excitation; lower curves, He I excitation) in a narrow energy range above $E_F$ measured with a resolution of 18 meV at the indicated sample temperatures.

Many properties of heavy-electron systems show two quite distinct regimes at temperatures far above and below $T_0$. This may be the most characteristic symptom pointing to the many-body nature of the anomalous low-temperature properties of this class of solids. It is a fundamental experimental challenge to investigate the evolution of the low-energy excitations concomitant to the transition between these two regimes. For increasing sample temperatures, Figs. 1(c)–1(f) display, in an enlarged view of the region extending from $E_F$ to 400 meV, the $4f^1$ spin-orbit–split final states excited with He II (upper curves) and He I (lower curves) radiation. The step between the data points is 5 meV and all spectra have been accumulated (3 h for He I excitation and 30 h for He II excitation) until $6\times10^3$ counts are obtained at 400 meV. At 15 K it is the instrumental resolution which sets the limit of the peak height at $E_F$. The break in the slope of the Fermi edge near the top of the peak [Fig. 1(c)] which appears to be shifted by about 35 meV towards higher energies is most likely caused by crystal-field splitting (see below). Unfortunately, the amplitude of this splitting in $CeSi_2$ has never been determined to the best of our knowledge. As the temperature increases, this first peak above $E_F$ is progressively washed out and has completely disappeared at 300 K where the thermal broadening of the Fermi edge is about 100 meV ($\sim 4k_BT$). The $4f^1_{7/2}$ final states around 280 meV form a rather symmetric peak at 15 K, which is also attenuated with increasing temperature but remains clearly visible.

In order to obtain a quantitative description of the temperature dependence of the excitation spectra, we have calculated the spectral functions for the Ander-

son Hamiltonian using the "slave boson" approach in the noncrossing approximation.[6,22] To reduce numerical problems in the low-temperature regime, the Boltzmann-weighted spectral functions were computed self-consistently according to Müller-Hartmann.[23] Since these functions have no simple analytic continuation, we do the self-consistent calculations on the real axis with an energy resolution of $1\times10^{-4}$ eV which is just sufficient at the lowest temperatures considered here. It should be noticed that the crystal-field (CF) splitting of the $j=\frac{5}{2}$ state has important consequences as already discussed for $CeAl_2$.[24] In the present case, for a tetragonal symmetry three doublets[25] are formed, thereby the ground-state degeneracy $N_f$ is lowered from 6 to 2. Since the existence of a CF splitting of $\Delta_{CF}=35$ meV between the ground state and the first excited doublet is compatible with the present data we have included such a CF splitting in our spectra calculation. For the interpretation of the present data it is sufficient to assume simply the degeneracy of the two excited $4f_{5/2}^1$ CF levels at 35 meV and of all $4f_{7/2}^1$ CF levels at $\Delta_{s.o.}=280$ meV so that the degeneracies of the ground state and the excited states are $N_f=2$, 4, and 8, respectively. The band is assumed to be centered at 0.5 eV above $E_F$ and to have a Gaussian shape of FWHM=3 eV. The spectrum shown in Fig. 1(b) represents the $f$ contribution to the excitation spectrum calculated with the parameters $T=15$ K, $\epsilon_f=-1.6$ eV, $\Delta=95$ meV, $\Delta_{s.o.}=280$ meV, $\Delta_{CF}=35$ meV, and a Gaussian broadening of 40 meV accounting for the instrumental resolution. With the single-impurity parameters deduced from this comparison we obtain $n_f=0.97$ for the $f$ occupation in the ground state and $\delta=3$ meV for the energy lowering resulting from a single-site hybridization, so that the corresponding Kondo temperature is $\delta/k_B=35$ K.

Figures 2(a)-2(d) show the $f$ contribution to the experimental spectra, obtained from the difference of the HeII and HeI excitation spectra [Figs. 1(c)-1(f)] weighted by the same cross-section ratio for all temperatures. These experimentally derived $f$ spectra are compared in Fig. 2 with the computed $f$-spectral functions [Figs. 2(e)-2(h)] for the corresponding sample temperatures with use of the same single-impurity parameters as above. The curves have been convoluted with Gaussians of 18 meV accounting for the instrumental resolution. Since the peak around 2 eV [Figs. 1(a) and 1(b)] shows practically no temperature dependence, only the spectral region of the $4f$ spin-orbit-split final states above $E_F$ is shown. Apart from the width of the experimental structures which is partly determined by lifetime broadening not included in the calculation, the agreement between experiment and model for the whole spectral range and for all temperatures is striking. It proves that this many-body calculation yields a correct description of the temperature dependence of our experimental spectra. The formation of the singlet ground state giving rise to

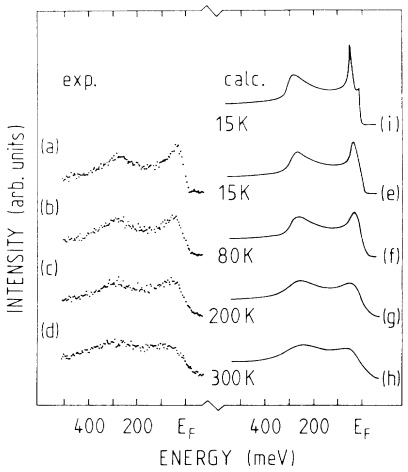


FIG. 2. Comparison between experimentally derived and computed $f$ spectra of $CeSi_2$. The curves (a)-(d) represent differences of the weighted spectra shown in Figs. 1(c)-1(f). The curves (e)-(h) are the result of a many-body calculation for the corresponding temperatures including $4f^1$ spin-orbit and $4f_{5/2}$ crystal-field splittings. A convolution with Gaussians of 18 meV FWHM has been performed in order to account for the finite instrumental resolution. The uppermost curve (i) represents the calculated $f$ spectrum for $T=15$ K without instrumental broadening.

the Kondo resonance close to $E_F$ requires a sharp cutoff in the occupation of the extended states and therefore can only develop at sufficiently low temperatures ($T\lesssim T_0$). When $k_BT$ increases and exceeds $k_BT_0$, nonsinglet states of higher energy become more and more populated so that the Fermi-liquid behavior transforms gradually into an atomiclike behavior. The spectra of Figs. 2(a)-2(d) yield the first unmistakable observation with photoemission of this progressive transition appearing as a collapse of the extremely narrow and intense distribution of the low-energy many-body excitations when the temperature is raised above $T_0$.

In general, for relatively small crystal fields such that the energy separation $\Delta_{CF}$ between ground state and the first excited doublet is of the order $\delta$ (CF=0) (obtained without CF), the Kondo peak remains the prominent feature of the photoemission spectrum near $E_F$.[24] For $\Delta_{CF}>\delta$ (CF=0), however, the Kondo temperature is reduced[26] and by a weight transfer from the Kondo peak the CF levels would become apparent in sufficiently well-resolved spectra. The present data of $CeSi_2$, recorded with a resolution of 18 meV, seem to be not too far from this situation, as indicated by the uppermost curve (i) in Fig. 2 representing the calculated spectrum for $T=15$ K without instrumental broadening. It remains that an important fraction of the intensity observed in the peak pinned at $E_F$ must be attributed to the many-body resonance formed of split-off states.[24] Their distribution reflects the weight of the $f$ character in the hy-

bridized basis states used in the simplest formulation of the singlet ground state at $T=0$ K.[27] In fact the many-body character of the peak at $E_F$ is also clearly demonstrated by its spectral weight at low temperature. If it would correspond to the excitation of single-particle states for which the Koopmans' approximation is valid, the integrated intensity of this peak alone should account for $n_f \approx 1$ instead of $n_f(1-n_f)=0.03$,[28] i.e., a factor of 30 larger than observed experimentally.

The flattening of the $f_{5/2}$ and $f_{7/2}$ structures when the temperature increases may seem to be in contradiction with the observation of a rather important peak located within 1 eV above $E_F$ in the x-ray photoemission spectrum of a $CeSi_2$ sample at 300 K.[19] The explanation of this situation must be looked for in the facts that the relative $f$ cross section increases substantially from 40-eV to 1500-eV photon energy and that at high temperature the $f_{5/2}$ and $f_{7/2}$ intensities are only spread in this energy range but have not vanished. When measured with the x-ray–photoemission–spectroscopy resolution of 300 meV it is then obvious that the corresponding intensity distribution has the appearance of a single peak located at $E_F$. This feature should not be confused with the Kondo peak which can only be observed at low temperature and with a sufficiently high resolution.

We would like to thank H. Beck for encouragement and advice, U. Mohr for the characterization of the sample, and the Swiss National Science Foundation for financial support.

[1]G. R. Stewart, Rev. Mod. Phys. **56**, 755 (1984).

[2]F. Steglich, J. Aarts, C. D. Bredl, W. Lieke, D. Meschede, W. Franz, and H. Schäfer, Phys. Rev. Lett. **43**, 1892 (1979).

[3]Z. Fisk, H. R. Ott, T. M. Rice, and J. L. Smith, Nature (London) **320**, 124 (1986).

[4]P. A. Lee, T. M. Rice, J. W. Serene, L. J. Sham, and J. W. Wilkins, Comments Condens. Matter Phys. **12**, 99 (1986).

[5]O. Gunnarsson and K. Schönhammer, Phys. Rev. Lett. **50**, 609 (1983), and Phys. Rev. B **28**, 4315 (1983).

[6]Y. Kuramoto, Z. Phys. B **53**, 37 (1983).

[7]N. Grewe, Z. Phys. B **53**, 271 (1983).

[8]F. Patthey, B. Delley, W.-D. Schneider, and Y. Baer, Phys. Rev. Lett. **55**, 1518 (1985).

[9]F. Patthey, S. Cattarinussi, W.-D. Schneider, B. Delley, and Y. Baer, Europhys. Lett. **2**, 883 (1986).

[10]W. H. Zachariasen, Acta Crystallogr. **2**, 94 (1949).

[11]W. H. Dijkman, A. C. Moleman, E. Kesseler, F. R. deBoer, and P. F. de Châtel, in *Valence Instabilities,* edited by P. Wachter and H. Boppart (North-Holland, Amsterdam, 1982), p. 515.

[12]H. Yashima and T. Satoh, Solid State Commun. **41**, 723 (1982).

[13]H. Yashima, H. Mori, T. Satoh, and K. Kohn, Solid State Commun. **43**, 193 (1982).

[14]Y. Onuki, Y. Shimizu, and T. Komatsubara, J. Phys. Soc. Jpn. **53**, 1210 (1984).

[15]G. R. Stewart, Z. Fisk, and M. S. Wire, Phys. Rev. B **30**, 482 (1984).

[16]F. Patthey, W.-D. Schneider, Y. Baer, and B. Delley, Phys. Rev. B **34**, 2967 (1986).

[17]V. T. Rajan, Phys. Rev. Lett. **51**, 308 (1983).

[18]G. Brauer and H. Haag, Z. Anorg. Allg. Chem. **267**, 198 (1952).

[19]E. Wuilloud, B. Delley, W.-D. Schneider, and Y. Baer, J. Magn. Magn. Mater. **47-48**, 197 (1985).

[20]S. M. Goldberg, C. S. Fadley, and S. Kono, J. Electron Spectrosc. Relat. Phenom. **21**, 285 (1981).

[21]J. M. Lawrence, J. W. Allen, S.-J. Oh, and I. Lindau, Phys. Rev. B **26**, 2362 (1982).

[22]P. Coleman, Phys. Rev. B **29**, 3035 (1984).

[23]E. Müller-Hartmann, Z. Phys. B **57**, 281 (1984).

[24]F. Patthey, W.-D. Schneider, Y. Baer, and B. Delley, Phys. Rev. B **35**, 5903 (1987).

[25]Satoh, Yashima, and Mori, in Ref. 11, p. 533.

[26]A. C. Hewson, D. M. Newns, J. W. Rasul, N. Read, H. U. Desgranges, and P. Strange, in *Theory of Heavy Fermions and Valence Fluctuations,* edited by T. Kasuya and T. Saso, Springer Series in Solid State Sciences Vol. 62 (Springer, Berlin, 1985), p. 134; O. Gunnarsson and K. Schönhammer, *ibid.*, p. 100.

[27]C. M. Varma and Y. Yafet, Phys. Rev. B **13**, 2950 (1976).

[28]O. Gunnarsson and K. Schönhammer, in *Handbook on the Physics and Chemistry of Rare Earths,* edited by K. A. Gschneidner, L. Eyring, and S. Hüfner (North-Holland, Amsterdam, 1987), Vol. 10.