Applicability of the Single Impurity Model to Photoemission Spectroscopy of Heavy Fermion Ce Compounds

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Photoemission spectra measured with an energy resolution of 5 meV from Ce-based heavy fermion materials are presented. The spectra add strong support to the interpretation of the peak at the Fermi level in terms of the spectral function calculated within the single impurity model. This work clearly demonstrates that if reliable information on heavy fermion compounds is to be obtained using photoemission spectroscopy, it is necessary to work with an instrumental resolution approaching kT_K, where T_K is the Kondo temperature. [S0031-9007(97)03272-9]

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Heavy fermions probably constitute the most widely studied class of highly correlated electron systems. When a rare earth is involved, the $4f$ states are weakly hybridized with the band states and at low temperature behave as an exceptionally narrow metallic band dominated by a very high correlation. In the Kondo description, the $4f$ local moment is gradually screened and a many-body singlet ground state is formed at $T = 0$ K. With increasing temperature, magnetic states become excited and the $4f$ states gradually recover their atomic character. The characteristic temperature separating these two regimes is the Kondo temperature, T_K, and $\delta = kT_K$, expressing the energy gain of the system per rare earth atom coming from the formation of the singlet state. The resulting unconventional properties (transport, magnetism, specific heat) are successfully predicted within the single impurity model (SIM), which is considered to contain the essential ingredients for describing the situation [1]. It has been particularly appealing to observe the states responsible for these manifestations in systems considered to be homogeneous dense Kondo compounds directly using electron spectroscopies. Calculations of spectral functions of these correlated systems based on the SIM [Gunnarsson-Schönhammer (GS) model [2], noncrossing approximation (NCA) [3]] differ markedly from the quasiparticle density of states, and they display signatures of the ambivalent nature of this many-body state; the high energy excitations account for its atomic character (bare energy of the $4f$ electrons and their intra-atomic Coulomb correlation energy), whereas the low-energy excitations display its exceptional metallic character generated by an extremely narrow renormalized band (Kondo peak) centered, for Ce compounds, above the Fermi level, E_F. In this model, δ completely characterizes the Kondo peak. Both the position of the peak and the weight of its occupied part are given by δ. The peak intensity at E_F scales with $1/\delta$.

In Ce-based heavy fermion systems, the Kondo energy scale, δ, typically ranges between 0.1 and 50 meV. This parameter thus sets extremely severe resolution conditions in photoemission studies. The most powerful technique for the disentanglement of the $4f$ states from the band states consists of the exploitation of synchrotron radiation to take advantage of the huge $4f$ cross section resonance at the Ce $4d$ threshold (120 eV). However, resolution limits in this energy range are currently of the order of 40 meV, and energy calibration with monochromatized radiation is not trivial. The other possibility commonly used to extract the $4f$ signal from photoemission spectra is offered by the conventional increase of the $4f$ cross section between the photon energies 21.2 eV (He I) and 40.8 eV (He II) delivered by He discharge lamps. These two intense lines have a very narrow natural width (≤2 meV), so that the resolution is essentially determined by the quality of the electron energy analysis. A few years ago, direct and inverse photoemission studies of Ce compounds produced spectra which seemed to demonstrate the essential characteristics of the spectral function based on the SIM [4,5]: the scaling of the Kondo peak intensity with T_K, and its nonconventional temperature dependence. This interpretation of the photoemission spectra has been disputed, however, with the claim that a conventional model provides a sufficient explanation for all photoemission observations [6–9]. This claim raises a very fundamental question which urgently needs to be cleared up [10,11], so that confidence in the capacity of photoemission to reveal many-body effects in correlated electron systems may be restored.

Recent technical improvements in the available electron spectrometers allow us now to achieve a total energy resolution of ~5 meV, a new condition which allows the relevant energy range δ containing the characteristic many-body excitations of moderately heavy fermions to be studied with more confidence. Our samples, prepared by *in situ* mechanical scraping or evaporation, can be cooled down to 12 K, and a base pressure of 5×10^{-11} Torr in the analysis chamber ensures an acceptable period of measurement time. Measurement of the Fermi edge width with our conditions gives directly the sample surface temperature. This was found to be limited at the low temperature end if loosely bound grains were allowed to remain on the surface. Photoemission being an extremely surface sensitive technique, in no event could the spectra be considered to account faithfully for bulk T_K. However, two essential parameters of the model are preserved in the surface region: the atomic symmetry of the states involved in the hybridization with the $4f$ states, and (at least approximately) the interatomic distances. The main changes are expected to originate from the local coordination of the Ce atoms. Monocrystalline surfaces certainly offer a much better defined situation with Ce atoms located in a restricted number of different sites, but this does not mean that the spectra are more representative of the bulk. A striking illustration of extreme surface effects is given by the very different $4f$ spectra close to E_F for the (100) and (110) faces of $CeBe_{13}$ [8]. Such effects are likely to be averaged on disordered surfaces, such as those prepared at low temperature in this work, and one can reasonably assume that qualitatively the low-energy $4f$ photoemission spectra remain related to the bulk T_K.

The aim of this study is to test the basic predictions of the spectral function of heavy fermion Ce compounds derived from the SIM with a significantly superior energy resolution than in previous studies. We have discarded Yb compounds, as these show such delicate surface preparation problems that different groups disagree on the experimental data [12–15], and U compounds, which are expected to show more complicated multiplet excitation spectra. In view of the surface problems discussed above, we will deliberately remain on a qualitative level which is quite sufficient to establish whether or not the data are compatible with the SIM.

Before presentation of our main results, we note that a reliable extraction of the $4f$ intensity from the subtraction of He I and He II photoemission spectra imperatively requires the same resolution for the two excitation lines and an accurate energy calibration of the spectra. The achievement of these two conditions by our instrumentation is demonstrated in Fig. 1(a). Here He I and He II spectra of the normal metal Nb measured at 12 K and those measured at 300 K are seen to coincide perfectly within the statistical noise.

Figure 1(b) shows our new high resolution He I and He II spectra from $CeSi_2$ within an energy region stretching to 400 meV below E_F. $CeSi_2$ offers favorable conditions for this study since its Kondo temperature, commonly accepted to be around 35 K [6,16], is located within the temperature range accessible to our experiment. In the He I excited spectrum the $4f$ cross section is very weak, so that only the other band states, which show no characteristic structure, are probed. At a photon energy of 40.8 eV, the $4f$ cross section increases markedly and the photoemission spectrum displays two salient structures commonly interpreted as accounting for the final state excitation of the spin-orbit split $4f_{7/2}$ component, located at 280 meV, and the occupied part of the Kondo peak, pinned at E_F. The FWHM of the Kondo peak, as determined from the difference spectrum in Fig. 1(d), is narrower by roughly a factor of 2 from our previous measurements.

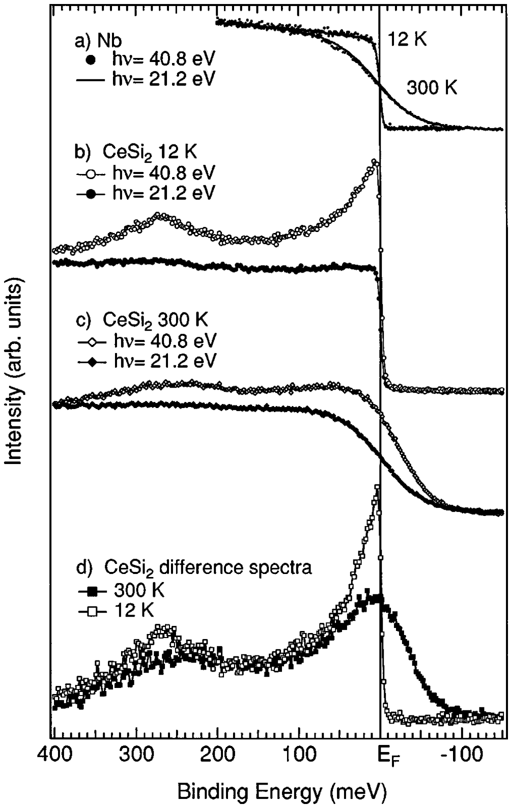

FIG. 1. (a) High resolution ($\Delta = 5$ meV) photoemission spectra of Nb recorded with He I and He II radiation at 12 and 300 K. (b) High resolution photoemission spectra recorded with He I and He II radiation from $CeSi_2$ at 12 K, and (c) at 300 K. (d) Difference spectra (He II − He I) of $CeSi_2$ at 12 and 300 K.

He I and He II spectra recorded from $CeSi_2$ at 300 K are shown in Fig. 1(c). Again the $4f$ structure is revealed in the He II spectrum, this time broadened in agreement with previous spectra. The spectra in Fig. 1(c) reveal an important aspect overlooked until now, however. The point at half-intensity of the edge in the He II spectrum is unambiguously located 20 meV above the Fermi level. This means that an anomalously high density of excited states just above E_F is thermally populated, a situation corresponding precisely to the existence of the nearly empty Kondo resonance of Ce systems. The exceptional character of this observation is enhanced in the difference spectrum at 300 K, shown in Fig. 1(d), where the centroide of the peak clearly moves toward the unoccupied states when the temperature increases.

In order to test the compatibility of our new spectra with the SIM, we have performed high resolution NCA calculations of the $4f$ spectral function at 12 and 300 K [4]. Two crystal field excitations as observed with neutron scattering [17] have been included ($\Delta_{\mathrm{CF}} = 25$ meV and 48 meV), and the hybridization strength has been adjusted in order to obtain a Kondo temperature for CeSi_2 of 35 K. The results of these calculations are shown in Fig. 2(a), with the difference spectra at 12 and 300 K from CeSi_2 reproduced in Fig. 2(b) for ease of comparison. Despite a less pronounced spin-orbit component in the predictions, the agreement between calculation and the difference spectra is extremely good, indeed almost perfect for the shape, width, and temperature dependence of the Kondo peak. Although some degree of caution must be exercised in making this comparison between a surface sensitive measurement and a calculation corresponding to the bulk, this demonstration seems to put beyond doubt that the SIM accounts for the basic spectral form.

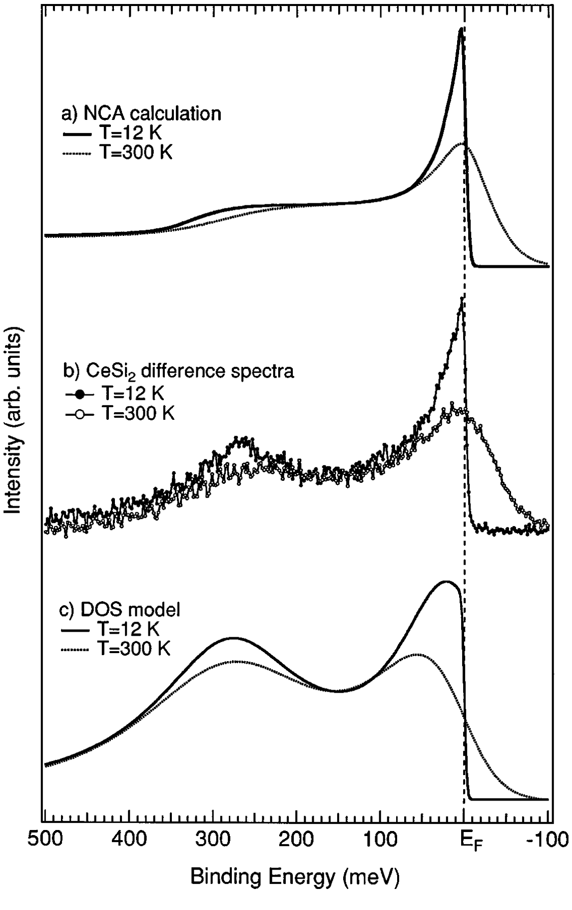

FIG. 2. (a) Noncrossing approximation calculation at $T = 12$ and 300 K, performed with the following parameters: Gaussian band of width 2 eV, centered at E_F; $\Delta_{\mathrm{hyb}} = 100$ meV; $\varepsilon_f = -1.2$ eV; $\Delta_{\mathrm{CF}} = 25$ meV, 48 meV; $U_{ff} = \infty$; $T_K = 35$ K (output). (b) Difference spectra (He II − He I) of CeSi_2 at 12 and 300 K. (c) A conventional DOS model following the prescription and using the parameters given in Ref. 6 (broadened by our experimental resolution of 5 meV).

In the light of our new data and the near perfect agreement with a SIM calculation, it is now necessary to test the reliability of the model claimed to be superior to SIM for analyzing the previous less well resolved photoemission spectra [6]. This consists of a conventional density of states (DOS) composed of two adjustable (position, width, and intensity) Lorentzians broadened by a phonon contribution and multiplied by the Fermi function. The same parameters as those used to fit the earlier CeSi_2 spectra have been adopted [6]. The calculated spectra, shown in Fig. 2(c), are at variance with the most characteristic features of the Kondo peak tail observed with photoemission [Fig. 2(b)]: at low temperature, the model peak is too broad, its top is rounded, and its maximum is located 20 meV below E_F; at 300 K, the peak moves toward higher binding energies and it is cut at approximately half intensity at E_F, as expected for a conventional DOS.

A clear scaling between the intensity of the photoemission peak pinned at E_F and the Kondo temperature has been observed in a series of very different compounds [4] and in CeSi_x ($2 \leq x \leq 1.6$) [18]. This conclusion is based on the comparison between theory and experiment of the intensity ratio variation of the $4f_{7/2}$ and Kondo peaks with T_K [4,18]. On the contrary, from different collections of spectra (including measurements of polycrystals and particular faces of single crystals measured with angular resolution), it has been inferred that this double-peaked structure is unrelated to T_K [6,9]. These spectra certainly demonstrate that a straight attribution of the bulk Kondo temperature to the measured surfaces is not valid, particularly when the preparation allows single-crystalline surfaces of compounds to reach thermodynamic equilibrium with composition and structure which might be markedly different from the bulk. With the aim of probing again with high resolution the existence of a correlation between the weight of the Kondo peak and T_K, we have measured well established Ce Kondo systems, excluding insulators and high temperature magnets, which span a wide range of T_K (α-Ce, CeSi_2, CeAl_3, CeSi_2, CeGe_2). In order to preserve their bulk characteristics as far as possible, they have been prepared by evaporation or mechanical cleaning at low temperature (12 K). Their low-energy (difference) spectra are displayed in Fig. 3, normalized approximately to the weight of the $4f_{7/2}$ component [4]. The spectra all have the same peaked shape sharply cut at E_F, and the systematic decrease in the weight of this Kondo peak with T_K is unmistakable, qualitatively confirming our earlier comparison with NCA calculations of less well-resolved spectra [4]. The main improvement is that the present resolution allows us to probe correctly the final states down to an energy scale of approximately 5 meV. This is still, however, not sufficient for the very heavy fermion systems CeAl_3 and CeCu_6, and for the latter the statistical noise in its weak difference spectrum becomes important. For CeGe_2, expected to show only a residual Kondo effect, the hump near E_F

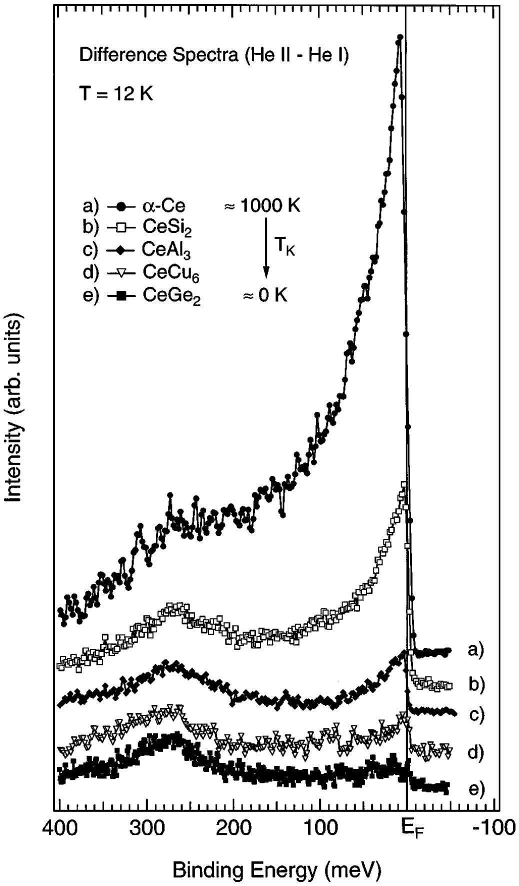

FIG. 3. Difference spectra (He II − He I) for a series of heavy fermion Ce compounds which span a wide range of T_K. The original spectra were recorded with high energy resolution ($\Delta = 5$ meV) and at 12 K.

is probably an artefact showing the limit of our subtraction technique for very weak $4f$ signals. We note that the FWHM of the peak decreases only by a factor of approximately 2 from α-Ce to CeCu$_6$ and does not reflect directly δ. We deliberately refrain from a quantitative analysis of the line shapes and intensities of the peaks since, quite apart from the difficulties involved in determining an absolute value for T_K, the spectra are measured from surfaces, at different values of T/T_K, and they certainly contain excitations of crystal field split levels and probably of phonons and electron-hole pairs.

In conclusion, this study presents photoemission data of some simple Ce-based Kondo compounds, demonstrating the necessity of an extremely high energy resolution. These new spectra are fully consistent with the SIM and cannot be analyzed with a conventional model. In the particular case of CeSi$_2$: (a) the peak at E_F cannot be accounted for by a DOS simulated by a Lorentzian line located 20 meV below E_F; (b) the linewidth and shape of the Kondo peak is consistent with a SIM calculation; and (c) the temperature dependence of this peak reflects the thermal population of the empty part of the Kondo resonance, in agreement with NCA calculations. In a series of simple heavy fermion compounds, it is seen that the Kondo temperature is a key parameter determining the weight of the Kondo peak and that an instrumental resolution approaching kT_K is essential if reliable information on heavy fermions is to be obtained. These conclusions are limited to the compounds measured in this study, but they do invite that the other data, used to suggest an approach different from SIM [9], be confirmed with better resolution.

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

[2] 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 (Elsevier Publisher, Amsterdam, 1987), Vol. 10, pp. 103-163.

[3] H. Keiter and Q. Qin, Physica B **163**, 594 (1990).

[4] F. Patthey, J.-M. Imer, W.-D. Schneider, H. Beck, Y. Baer, and B. Delley, Phys. Rev. B **42**, 8864 (1990).

[5] D. Malterre, M. Grioni, and Y. Baer, Adv. Phys. **45**, 299 (1996).

[6] J. J. Joyce, A. J. Arko, J. Lawrence, P. C. Canfield, Z. Fisk, R. J. Bartlett, and J. D. Thompson, Phys. Rev. Lett. **68**, 236 (1992).

[7] J. J. Joyce, A. J. Arko, J. M. Lawrence, J. Tang, P. C. Canfield, R. J. Bartlett, Z. Fisk, J. D. Thompson, and P. S. Riseborough, Solid State Commun. **83**, 551 (1992).

[8] A. B. Andrews, J. J. Joyce, A. J. Arko, Z. Fisk, and P. S. Riseborough, Phys. Rev. B **53**, 3317 (1996).

[9] A. J. Arko, J. J. Joyce, A. B. Andrews, J. D. Thompson, J. L. Smith, E. Moshopoulou, Z. Fisk, A. A. Menovsky, P. C. Canfield, and C. C. Olson, Physica B **230–232**, 16 (1997).

[10] J. W. Allen and O. Gunnarsson, Phys. Rev. Lett. **70**, 1180 (1993).

[11] J. J. Joyce and A. J. Arko, Phys. Rev. Lett. **70**, 1181 (1993).

[12] L. H. Tjeng, S.-J. Oh, E.-J. Cho, H.-J. Lin, C. T. Chen, G.-H. Gweon, J.-H. Park, J. W. Allen, T. Suzuki, M. S. Makivić, and D. L. Cox, Phys. Rev. Lett. **71**, 1419 (1993).

[13] P. Weibel, M. Grioni, D. Malterre, B. Dardel, Y. Baer, and M. J. Besnus, Z. Phys. B **91**, 337 (1993).

[14] R. I. R. Blyth, J. J. Joyce, A. J. Arko, P. C. Canfield, A. B. Andrews, Z. Fisk, J. D. Thompson, R. J. Bartlett, P. Riseborough, J. Tang, and J. M. Lawrence, Phys. Rev. B **48**, 9497 (1993).

[15] J. M. Lawrence, A. J. Arko, J. J. Joyce, P. C. Canfield, Z. Fisk, J. D. Thompson, and R. J. Bartlett, J. Magn. Magn. Mater. **108**, 215 (1992).

[16] F. Patthey, W.-D. Schneider, Y. Baer, and B. Delley, Phys. Rev. Lett. **58**, 2810 (1987).

[17] R. M. Galera, A. P. Murani, and J. Pierre, Physica B **156&157**, 801 (1989).

[18] D. Malterre, M. Grioni, P. Weibel, B. Dardel, and Y. Baer, Phys. Rev. B **48**, 10 599 (1993).