Evidence of a Kondo Scale from the Temperature Dependence of Inverse Photoemission Spectroscopy of $CePd_3$

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Inverse photoemission spectra have been measured as a function of temperature in $CePd_3$. Although the experimental energy resolution is 1 order of magnitude larger than the characteristic thermodynamic energy scale of this system, a temperature dependence of the spectral function is observed. This result proves that high-energy spectroscopies are sensitive to the breakdown of the Kondo state as the low-lying magnetic states become thermally populated.

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Electronic correlations play a fundamental role in the physical properties of solids [1,2]. Although weakly correlated systems like simple metals are well described in terms of itinerant electron bands, a localized description becomes more appropriate for strongly correlated materials. Rare-earth systems represent the limiting case of very large intra-atomic Coulomb interactions with atomiclike $4f$ states. However, in several cerium compounds, unusual properties are observed resulting from the competition between the correlations of the f electrons and their hybridization with conduction states [3,4]. At low temperature, these systems behave like Fermi liquids but above a characteristic temperature (the Kondo temperature T_K) a progressive evolution to a localized behavior takes place [5]. The Kondo energy ($\delta = k_B T_K$), which represents the splitting between the singlet ground state and the low-lying magnetic states, determines the scaling behavior of the physical properties. For example, the magnetic susceptibility is temperature independent for $T \ll T_K$, it exhibits a broad maximum around T_K, and for $T \gg T_K$ it follows a Curie-Weiss law reflecting the formation of a local moment as magnetic excited states become thermally populated.

High-energy spectroscopic techniques are particularly useful in revealing the correlations since their strength is related to the energy positions of satellite structures [6-8]. Nevertheless, such techniques under standard conditions have never revealed the low-energy scale which governs the thermodynamic properties. To the best of our knowledge, the only spectroscopic investigation of the thermal excitations in a Kondo system was the high-resolution photoemission study of $CeSi_2$ [9]. This study showed a temperature dependence of the spectral function just below the Fermi energy (E_F). In the framework of the single impurity Anderson model, the intensity at E_F in the photoemission spectrum reflects the tail of the Kondo resonance which develops in the spectral function at energy δ above E_F. This resonance results from the formation of a singlet ground state and it is expected to be strongly reduced as excited magnetic states become thermally populated (for temperatures above T_K) [10-12]. This effect in photoemission is subtle and has been recently called into question [13]. However, as the main weight of the Kondo resonance is located above E_F, the $N+1$ (electron addition) part of the spectral function, which is probed by bremsstrahlung isochromat spectroscopy (BIS), should be more sensitive to the temperature dependence of the Kondo effect. In this paper we show for the first time that the $4f$ BIS spectral function exhibits an important temperature dependence despite the fact that the state-of-the-art experimental resolution is more than 1 order of magnitude larger than the Kondo energy. This result definitely establishes that high-energy spectroscopies give information on the energy scale responsible for the thermodynamic properties.

$CePd_3$ is a good candidate for this investigation. Previous high-energy spectroscopy experiments [14-17] on this system have shown a significant $4f$ configuration admixture in the ground state. Moreover, resistivity and magnetic measurements [18,19] suggest a Kondo temperature around 240 K. $CePd_3$ has been prepared by arc-melting the constituent materials several times under argon atmosphere. X-ray powder diffraction patterns have confirmed the single phase nature with the $AuCu_3$ structure of the sample. BIS spectra have been obtained with a photon energy of 1486.6 eV and a total energy resolution of 0.6 eV was achieved. The sample could be cooled with a closed-cycle He refrigerator at about 15 K. The pressure was in the low 10^{-10}-Torr range. Clean samples were obtained by scraping the surface with a diamond file, and the surface cleanliness was regularly checked by photoemission.

Figure 1 shows the BIS spectrum of $CePd_3$ for $T=15$ and 300 K. The room-temperature spectrum is in good agreement with previously reported data [20,21]. The spectra are dominated by the $4f$ contribution which results in a narrow peak just above the Fermi energy and a broad structure centered at about 5 eV. The additional peak at 2.2 eV was interpreted to be the cerium $5d$ split-off band and it is encountered in many XPd_3 compounds (X=rare earth, yttrium) [21,22]. These different features are superimposed to a broad, structureless sp band as clearly illustrated by the BIS spectrum of YPd_3 [21]. The intensities of the two spectra have been normalized at the highest energy (8.5 eV) where the $4f$ signal vanishes. In order to isolate the $4f$ excitations, we

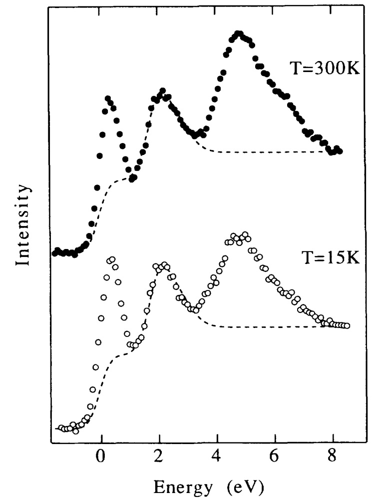

FIG. 1. BIS spectra of the CePd$_3$ compound at $T=15$ K (open circles) and $T=300$ K (solid circles). The dashed lines are the assumed non-f contribution and inelastic background.

have simulated the contributions of non-f states and of the inelastic background by a simple analytical function (dashed curve in Fig. 1) reproducing the BIS spectrum of YPd$_3$ [21]. We are aware that this procedure is somewhat arbitrary but, for the purpose of demonstrating the temperature evolution of the spectra, the most important point is to assume exactly the same function in both spectra since no mechanism predicts a sizable temperature dependence of these contributions. A simple inspection of the raw data reveals unambiguously that between 15 and 300 K the relative intensity of the two $4f$ features is markedly modified. This is more clearly demonstrated in Fig. 2(a) where the $4f$ intensities obtained from Fig. 1 are reported for the two temperatures and normalized for clarity to the maximum of the high-energy structure.

The presence of well-separated structures in the BIS spectra reflects many-body or dynamical effects and can be easily understood in the framework of the Gunnarsson-Schönhammer (GS) model [8]. The zero-temperature spectrum can be calculated with this variational approach. The BIS spectral function corresponds to transition from the ground state (N particle state) toward the $N+1$ particle excited states. The high-energy structure represents the final states of $4f^2$ character, its position is determined by the intra-atomic Coulomb interaction U_{ff} and the $4f$ energy ε_f. On the other hand, the peak just above the Fermi energy (the $4f^1$ final states) is mainly composed of two contributions: the Kondo resonance at $\delta=k_BT_K$ and the spin-orbit satellite at $E=\delta+\Delta_{\text{s.o.}}$ ($\Delta_{\text{s.o.}}=280$ meV in cerium) [12]. As a result of the limited experimental resolution of the technique, these two latter structures are not experimentally resolved and only one peak about 0.8 eV wide is observed.

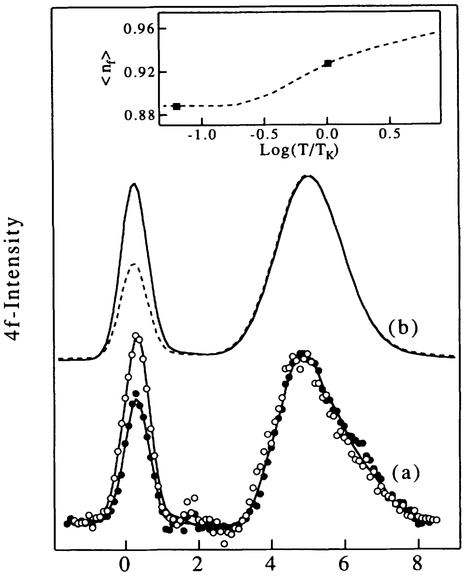

FIG. 2. (a) $4f$-BIS spectral function normalized to the intensity maximum of the high-energy structure for two temperatures $T=15$ K (open circles) and $T=300$ K (solid circles) obtained by removing a background from the experimental spectra. The solid lines are a guide for the eye. (b) Calculated $4f$ spectral function normalized to the intensity maximum of the high-energy structure for $T=0$ K (solid line) and $T=300$ K (dashed line). The peaks near E_F were convoluted by a Gaussian (0.7 eV FWHM) to account for the experimental resolution and the high-energy structure ($4f^2$ final states) was broadened by a Gaussian (2 eV FWHM) to account for the multiplet effect. The $T=0$ K spectrum is calculated in the Gunnarsson-Schönhammer model with the following parameters: $U_{ff}=5.7$ eV, $\varepsilon_f=-1.5$ eV, $\Delta_{\text{s.o.}}=2.80$ meV, and $\Gamma=90$ meV. Inset: A NCA calculation of the mean value of the $4f$ occupation number as a function of temperature. The two black squares represent the calculated values of $\langle n_f\rangle$ for $T=15$ and 300 K.

At finite temperature, this picture is modified. As the available final states do not depend on temperature, the variation of the spectral function results from the modification of the initial state: At $T=0$ K, the initial state is the singlet ground state but it becomes a statistical admixture involving multiplet excited states at $T\neq 0$ K. The finite-temperature spectrum cannot be obtained in the GS approach; however, the low-energy peak can be calculated in the noncrossing approximation (NCA) of the infinite U_{ff} degenerate Anderson model [10–12]. In this formalism, a temperature dependence of the spectral function is expected. The low-energy structures, composed of the Kondo and the spin-orbit resonances, are both strongly depleted when the temperature increases from $T\ll T_K$ to $T\gg T_K$. On the contrary, the $N-1$ part of the density of states is less sensitive to temperature effects. The weight of the photoemission spectrum (PES) is nearly constant [23] although the shape near E_F varies with temperature as experimentally shown by the high-resolution photoemission study of CeSi$_2$ [9]. This contrasted behavior of PES and BIS spectra results from the different nature of the final states in the two spectroscopies [12]. The structures at $E=\delta$ and $E=\delta+\Delta_{\mathrm{s.o.}}$ in the BIS spectrum are associated with $4f^1$ final states with negligible $4f^0$ admixture. As the thermally excited states have also a predominantly $4f^1$ character, the coupling with these $4f^1$ BIS final states, which is determined by the matrix elements $\langle N+1|a_f^\dagger|\Psi_{\mathrm{ex}}\rangle$, is negligible. $|\Psi_{\mathrm{ex}}\rangle$ is a thermal excited state, $a_f^\dagger$ the creation operator of a $4f$ electron, and $|N+1\rangle$ a final state of BIS. Therefore, the thermal population of the excited states increases only the $4f^2$ peak whereas the corresponding loss of statistical weight of the ground state decreases the $4f^1$ peak. On the other hand, the photoemission final states $|N-1\rangle$ at E_F and $E=-\Delta_{\mathrm{s.o.}}$ have a $4f^0$-$4f^1$ admixture similar to that in the ground state and, therefore, the spectral intensity is determined by the weight of the f^1 configuration in the initial state and f^0 configuration in the final states. As the f^1 contributions in the ground and excited states are roughly the same, the spectral weight in photoemission has a much weaker temperature dependence than the BIS part.

In order to simulate the spectral function for finite temperatures and U_{ff}, we use a phenomenological procedure. First, we calculate the mean value of the $4f$ occupation number $\langle n_f\rangle$ as a function of temperature in the NCA (inset of Fig. 2). For a Kondo temperature of $T_K=240$ K, $\langle n_f\rangle$ increases from $n_{f,\mathrm{g.s.}}=0.89$ at $T\rightarrow 0$ to $\langle n_f\rangle=0.93$ at room temperature. This evolution reflects the progressive population of the low-lying excited states with $n_{f,\mathrm{ex}}\approx 1$ as T increases. Then, we determine the respective populations, $a(T)$ and $b(T)$, of the ground and excited states in the initial statistical admixture from the calculated value of the $4f$ occupation number at T: $\langle n_f\rangle(T)=a(T)n_{f,\mathrm{g.s.}}+b(T)n_{f,\mathrm{ex}}$. The finite-temperature spectra are simply calculated from a combination of the BIS spectra corresponding to the ground and excited states weighed by their respective population in the initial state:

$$A(\omega,T)=a(T)A_{\mathrm{GS}}(\omega)+b(T)A_{\mathrm{ex}}(\omega)\,, \qquad (1)$$

where $A_{\mathrm{GS}}(\omega)$ is the $T=0$ K spectrum calculated in the Gunnarsson-Schönhammer model [8] and $A_{\mathrm{ex}}(\omega)$ is the calculated spectrum for a $4f^1$ initial state, which only exhibits the high-energy structure corresponding to $4f^2$ final states.

Then, with increasing temperature, there is an intensity transfer from the $4f^1$ to the $4f^2$ peak but, in order to make easier the comparison with experiment, the calculated $4f$ spectral functions have been normalized to the maximum of the $4f^2$ structure [Fig. 2(b)]. The effect of temperature is well described within our simple approach but it is slightly overestimated. Experimental and theoretical arguments could explain the small differences between measured and calculated finite-temperature spectral functions. The presence of the split-off band structure in the BIS spectra prevents a very accurate determination of the $4f$ intensity in the experimental spectra. Moreover, the value of $\langle n_f\rangle$ is calculated in the infinite U_{ff} limit; finite U_{ff} can introduce a slight modification of the $\langle n_f\rangle$ temperature dependence. These small differences can also result from the technique itself. Recently, it has been demonstrated that the cerium valence at the surface in $\mathrm{CePd_3}$ is nearly trivalent ($n_f=0.99$) and strongly differs from the bulk value ($n_f=0.85$) [24]. This different valence at the surface mainly results from a modification of the coordination and then should be temperature independent. The surface contribution leads to a reduction of the experimental temperature effect and should be taken into account in an accurate quantitative analysis. Despite these limitations, the BIS spectral function clearly exhibits a temperature dependence revealing unambiguously a Kondo energy scale in the electronic properties. Recently, it was proposed that the f electrons in hybridized systems like α-Ce can be described in a one-electron band model [25]. Such temperature-dependent spectroscopic behaviors can hardly be reconciled with a band picture of the $4f$ electrons and then strongly support the description of f states in terms of an impurity many-body model [26].

To summarize, this study shows an indisputable temperature dependence of the spectral function. As the BIS $4f^1$ structure is composed of the Kondo and spin-orbit resonances which are both depleted with increasing temperature through the low-energy scale T_K, our measurements show the same progressive evolution from a Fermi liquid to a localized behavior exhibited by near-ground-state properties such as magnetic susceptibility, specific heat, resistivity, etc. As a consequence, the ground-state parameters of the Anderson model, which have been derived from room-temperature XPS or BIS experiments without considering this important temperature effect, will have to be critically reviewed. Our results also demonstrate that even with a resolution 1 or 2 orders of magnitude worse than the low-energy scale (k_BT_K), BIS reflects the subtle modification of the initial state with temperature and offers a new tool for the investigation of the unconventional physical properties of hybridized $4f$ systems.

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[1] P. Fulde, Prog. Theor. Phys. **80**, 47 (1984).
[2] S. Hüfner, in *Photoemission in Solids II*, edited by L. Ley and M. Cardona (Springer-Verlag, Berlin, 1979), Vol. 27, p. 173.
[3] J. M. Lawrence, P. S. Riseborough, and R. D. Parks, Rep. Prog. Phys. **44**, 1 (1981).
[4] P. A. Lee, T. M. Rice, J. W. Serene, L. J. Sham, and J.

W. Wilkins, Comments Condensed Matter Phys. **12**, 99 (1986).

[5] P. Nozières, J. Low Temp. Phys. **17**, 31 (1974).

[6] A. Kotani, in *Handbook of Synchrotron Radiation*, edited by G. V. Marr (Elsevier, Amsterdam, 1987), Vol. 2, p. 611.

[7] J. W. Allen, S. J. Oh, O. Gunnarsson, K. Schönhammer, M. B. Maple, M. S. Torikachvili, and I. Lindau, Adv. Phys. **35**, 275 (1986).

[8] O. Gunnarsson and K. Schönhammer, Phys. Rev. B **28**, 4315 (1983).

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

[10] H. Kojima, Y. Kuramoto, and M. Tachiki, Z. Phys. B **54**, 293 (1984).

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

[12] N. E. Bickers, D. L. Cox, and J. W. Wilkins, Phys. Rev. Lett. **54**, 230 (1985); Phys. Rev. B **36**, 2036 (1987).

[13] J. Joyce, A. J. Arko, R. J. Bartlett, C. Canfield, Z. Fisk, J. Lawrence, and J. Tang, Bull. Am. Phys. Soc. **36**, 460 (1991).

[14] F. U. Hillebrecht, J. C. Fuggle, G. A. Sawatzky, M. Campagna, O. Gunnarsson, and K. Schönhammer, Phys. Rev. B **30**, 1777 (1984).

[15] J. C. Fuggle, F. U. Hillebrecht, Z. Zolnierek, R. Lässer, Ch. Freiburg, O. Gunnarsson, and K. Schönhammer, Phys. Rev. B **27**, 7330 (1983).

[16] E. Wuilloud, W.-D. Schneider, B. Delley, Y. Baer, and F. Hullinger, J. Phys. C **17**, 4799 (1984).

[17] R. D. Parks, S. Raen, M. L. denBoer, V. Murgai, and T. Mihalisin, Phys. Rev. B **28**, 3556 (1983).

[18] J. M. Lawrence, J. D. Thompson, and Y. Y. Chen, Phys. Rev. Lett. **54**, 2537 (1985).

[19] J. Aarts, F. R. deBoer, P. F. de Châtel, and A. Menovsky, Solid State Commun. **56**, 623 (1985).

[20] Y. Baer, H. R. Ott, J. C. Fuggle, and L. E. De Jong, Phys. Rev. B **24**, 5384 (1981).

[21] F. U. Hillebrecht, J. C. Fuggle, G. A. Sawatzky, and R. Zeller, Phys. Rev. Lett. **51**, 1187 (1983).

[22] C. Koenig and M. A. Khan, Phys. Rev. B **38**, 5887 (1988).

[23] O. Gunnarsson and K. Schönhammer, in *Handbook on the Physics and Chemistry of Rare-Earths*, edited by K. A. Gschneidner, Jr., L. Eyring, and S. Hüfner (North-Holland, Amsterdam, 1987), Vol. 10, p. 103.

[24] C. Laubschat, E. Weschke, C. Holtz, M. Domke, O. Stebel, and G. Kaindl, Phys. Rev. Lett. **65**, 1639 (1990).

[25] O. Eriksson, R. C. Albers, A. M. Boring, G. W. Fernando, Y. G. Hao, and B. R. Cooper, Phys. Rev. B **43**, 3137 (1991).

[26] Y. Baer, M. Grioni, D. Malterre, and W.-D. Schneider, Phys. Rev. B **44**, 9108 (1991).