

Resonant Inverse Photoemission: A New Probe of Correlated Systems

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Inverse photoemission measurements of cerium compounds reveal a strong energy dependence near the Ce M_5 ($3d_{5/2} \rightarrow 4f$) absorption edge. Two separate resonances, resulting from configuration mixing in the ground state, are identified for the first time. Their relative intensities reflect the different hybridization strengths in various Ce-based materials. Because of its site and symmetry selectivity, resonant inverse photoemission is potentially a valuable technique for the investigation of correlated materials, complementary to the well-established resonant photoemission spectroscopy.

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High-energy spectroscopies play a prominent role in the investigation of valence fluctuation in cerium compounds [1-7]. They have contributed to identifying the partially localized character of the strongly correlated Ce $4f$ electrons and to establishing a description of these electronic states based on the degenerate Anderson impurity model [8-10]. Photoemission (PES) and inverse photoemission (IPES) spectroscopy can in principle be interpreted as the many-body spectral function derived from the Anderson Hamiltonian. A reliable analysis of the experimental results, however, depends on the ability to separate the $4f$ contribution from that of other electronic states. In PES, this crucial problem is usually tackled by comparing spectra at various excitation energies, to take advantage of the different energy dependence of the photoionization cross section for the $4f$ and the band states. Unfortunately, in many Ce systems an unambiguous determination of the $4f$ spectral weight is hindered by a large band contribution [11]. The development of resonant PES (RESPES), which exploits the occurrence of resonances in the $4f$ cross section when the photon energy is tuned to an appropriate absorption edge, has provided a clear breakthrough in this field. Because of the localized nature of the core hole, and to the dipole selection rules, RESPES spectra obtained at the Ce $N_{4,5}$ ($4d$)⁴ and $M_{4,5}$ ($3d$) edge [12] essentially reflect the $4f$ contribution at the Ce site, and have recently been interpreted within the framework of the Anderson model [13].

Conventional inverse photoemission measurements are traditionally performed either in the vacuum ultraviolet (VUV) range ($5 < h\nu < 30$ eV) or at the Al K_α characteristic energy (1486.6 eV). IPES spectra of Ce compounds measured at the lower end of the VUV range are dominated by emission from band states. In the x-ray region the $4f$ signal is clearly visible, but the subtraction of the non- f and inelastic background is not always straightforward. Moreover, the IPES cross section is by orders of magnitude smaller than the corresponding PES cross section [14], which imposes long measuring times and rules out the investigation of interesting samples like diluted materials or adsorbates. It would be highly desirable to improve this situation by exploiting resonances of the

IPES cross section.

The existence of a resonant enhancement of the bremsstrahlung emission was first demonstrated by the pioneering work of Liefeld, Burr, and Chamberlain [15] and Riehle [16] on metallic La and Ce. Resonances were later observed also in Ni and Sc in the x-ray [17] and VUV [18] range. The early results [15,16], however, as well as subsequent theoretical [19] and experimental [20] work, were mainly concerned with the case of f^0 La, and spectra of metallic Ce were interpreted with the assumption of integer valence. This conceptual limitation, as well as the technical difficulties of the experiment, prevented resonant IPES from ever being considered as a spectroscopic probe of valence fluctuators. In every respect the situation is different today. In the last decade important advances have been made in the understanding of the ground state and spectral properties of Ce materials. Significant improvements, fostered by the development of synchrotron radiation beam lines, have also been achieved in the monochromatization and detection of soft x rays. In this Letter we demonstrate the potentialities of resonant IPES (RIPES) which now appears as a promising new tool for investigating the electronic properties of Ce compounds, on the same footing as RESPES.

The RIPES measurements were performed near the Ce M_5 absorption edge (883 eV) in a dedicated IPES spectrometer. Electrons were generated by an electron gun equipped with an indirectly heated BaO cathode. The kinetic energy of the electrons $E_K \sim V_c + \Phi$, where $\Phi \sim 2.5$ eV is the work function of the BaO cathode, could be varied continuously by adjusting the cathode voltage. The width of the electron distribution was 0.3-0.5 eV. The emitted photons were dispersed by a Bragg reflection on a beryl (10 $\bar{1}$ 0) crystal onto a microchannel plate detector equipped with a resistive anode encoder. The theoretical energy resolution of the spectrograph, determined by the crystal's rocking curve, is approximately 0.4 eV at the Ce M_5 edge. The actual resolution is determined by the size of the illuminated area on the sample, which acts as the entrance slit of the monochromator. Experiments were carried out with a total energy resolution (electrons plus photons) of ~ 0.6 -0.8 eV. Poly-

crystalline samples prepared in an arc furnace were cleaned *in situ* by scraping with a diamond file at a base pressure of 1×10^{-10} torr, and measured at room temperature.

Within the framework of the Anderson model the $4f$ IPES spectral function of a Ce impurity is predicted to exhibit peculiar features that reflect the hybrid character of the singlet ground state. In the limit of large Coulomb repulsion the ground state has, in simplified notation, the form $|\Psi_G\rangle = a|f^0\rangle + b|f^1\rangle$, where f^0 and f^1 indicate configurations of the Ce impurity with zero and, respectively, one $4f$ electron. The addition of one $4f$ electron in an IPES experiment couples the f^0 and f^1 configurations of the (N -electron) ground state $|\Psi_G\rangle$ to the f^1 and f^2 character of ($N+1$)-electron final states. Symbolically we indicate these transitions as $|f^0\rangle + e^- \rightarrow |f^1\rangle + h\nu$, and $|f^1\rangle + e^- \rightarrow |f^2\rangle + h\nu$. The former generate a sharp peak near the Fermi level (the "Kondo peak"), with spin-orbit and crystal field satellites. The latter yield a structure, broadened by multiplet effects, 4–5 eV above E_F . Because of the limited experimental energy resolution of IPES, the Kondo peak and its satellites cannot be resolved, and appear as a single peak. The intensity of this peak is proportional to the weight of the f^0 configuration in the ground state, and is therefore a sensitive indicator of hybridization. In addition to this normal IPES process, when the excitation energy reaches the $3d$ absorption edge of Ce, new transitions from $|\Psi_G\rangle$ that involve the creation of a $3d$ core hole (\underline{c}) become possible:

$$|f^0\rangle + e^- \rightarrow |\underline{c}f^2\rangle \rightarrow |f^1\rangle + h\nu, \quad (1)$$

$$|f^1\rangle + e^- \rightarrow |\underline{c}f^3\rangle \rightarrow |f^2\rangle + h\nu. \quad (2)$$

Since these transitions have the same initial state ($|\Psi_G\rangle$) and the same final states as the normal IPES transitions, quantum interference with the direct processes must produce resonances in the transition rates [21]. A strong

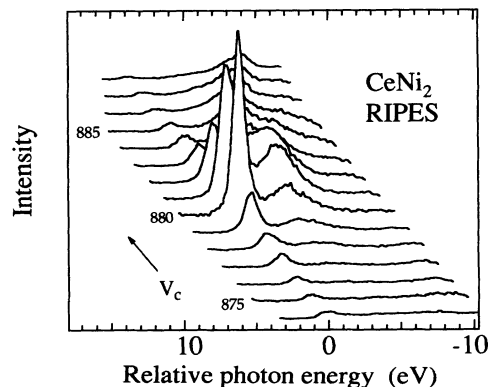


FIG. 1. Inverse photoemission spectra of CeNi₂ collected at various excitation energies through the Ce M_5 ($3d_{5/2}$) absorption edge. The spectra are labeled by the accelerating voltage of the primary electron beam. The photon energy zero was arbitrarily set.

enhancement of the whole spectrum can therefore be anticipated at the edge energy.

In order to test this prediction, we have performed an energy dependent investigation of CeNi₂, a compound characterized by a rather strongly hybridized ground state, with an estimated Kondo temperature $T_K \sim 900$ K [4]. Figure 1 shows a set of IPES spectra of CeNi₂, collected around the Ce M_5 edge, and labeled by the accelerating cathode voltage V_c . At the lowest excitation energy ($V_c = 874$ eV) the signal level was comparable to that of conventional IPES spectra obtained at 1486 eV in our laboratory. Spectral features, however, can be barely distinguished on the scale of Fig. 1. Increasing the electron energy has two clear effects on the IPES spectra: a corresponding shift to higher photon energy, and a dramatic resonant enhancement of 2 orders of magnitude around 880 V.

The comparison, in Fig. 2, of the 880 and 882 V spectra, shows that the IPES spectral intensity is not uniformly enhanced at resonance. The 880 V spectrum is dominated by the f^1 peak near E_F , and the f^1/f^2 ratio is considerably larger than in a conventional IPES spectrum (inset). The ratio between the $4f$ signal and the non- f and inelastic background (B) is also strongly increased, demonstrating the sensitivity of RIPES to the $4f$ states. The separation between the f^1 peak and the center of the f^2 structure is smaller than in the IPES spectrum at 1486 eV, and it increases between 880 and 882 V. At 882 V the f^1 signal is reduced to about 30% of its resonance value, and the f^2 intensity has roughly doubled. Between the f^1 and f^2 peaks in the 882 V spectrum, we observe the characteristic Ce M_α line that corresponds to the transitions

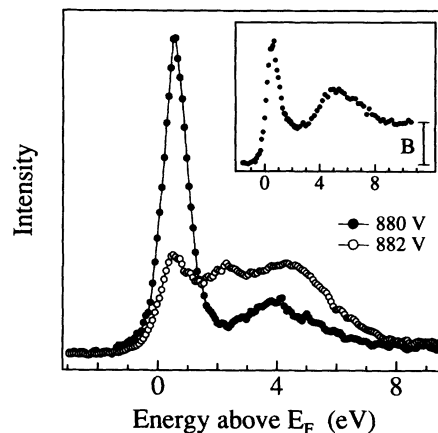


FIG. 2. RIPES spectra of CeNi₂ from Fig. 1, corresponding to the maximum of the f^1 (880 V) and f^2 (882 V) emission. At variance with Fig. 1, the spectra have been shifted with respect to each other to compensate for the different primary energy. The intermediate feature visible at 882 V is the characteristic Ce M_α line. Inset: Conventional IPES spectrum ($h\nu = 1486$ eV) of CeNi₂.

$$|f^1\rangle + e^- \rightarrow |cf^2k\rangle \rightarrow |f^1k\rangle + hv^*, \quad (3)$$

where k represents a conduction band electron. The M_a line is degenerate with the f^1 peak at threshold and drifts away from the f^1 peak with increasing excitation energy. This behavior is therefore analogous to that of characteristic Auger emissions in resonant PES.

We have separately measured the primary energy dependence of the f^1 and f^2 peaks by integrating the IPES signal within two windows (respectively, 2.5 and 5 eV wide) that tracked the position (i.e., the photon energy) of the two peaks on the detector. The resulting constant final state curves (CFS) of Fig. 3 demonstrate that the two spectral features resonate at distinct energies, separated by ~ 2 eV. This value is in very good agreement with our simple model that predicts a separation $\Delta E = E(cf^3) - E(cf^2) \sim \epsilon_f + 2U_{ff} + U_{fc} \sim 2$ eV, where $E(cf^3)$ and $E(cf^2)$ represent the energies of the two intermediate-state configurations, and where we have used typical values for the $4f$ energy ϵ_f (-2 eV), the f - f Coulomb repulsion U_{ff} (7 eV), and the core hole- $4f$ Coulomb interaction U_{fc} (-10 eV).

A quantitative analysis of the resonance profiles would require an elaborate treatment of the RIPES process, which takes into account the multiplet structure, hybridization, and coupling of the relevant configurations. Such a calculation is clearly beyond the scope of this Letter. We just remark that the widths of both the f^1 (2 eV) and the f^2 (4 eV) CFS curves are considerably narrower than the cf^2 and cf^3 manifolds, that extend over many eV's. We interpret this sharpening as a consequence of selection rules that limit, in the excitation [22] and especially in the deexcitation [23] processes, the number of allowed transitions.

The high sensitivity of RIPES to the nature of the ground state is illustrated by the comparison of different Ce materials. The $4f$ electrons are weakly hybridized in CeSb, which orders below 16 K with a magnetic moment close to that of a free Ce^{3+} ion [24]. Core level PES results [3], as well as conventional IPES [25] and high-resolution PES, also indicate a very small hybridization. The CFS curves of Fig. 3 demonstrate a striking difference with respect to CeNi₂, since the f^2 peak dominates a very weak " f^1 " structure. Minor differences concern the smaller separation of the two maxima and the width of the f^2 CFS (3.25 eV). The vanishingly small intensity in the $f^0 \rightarrow f^1$ channel is consistent with an almost pure f^1 ground state configuration. We believe that the weak " f^1 " feature essentially reflects the M_a emission (3), whose intensity is not related to the weight of the f^0 configuration. Since the M_a emission yield is not expected to be very different in CeNi₂ and CeSb, its small intensity in CeSb justifies the decision to neglect it also in CeNi₂. The variation of the f^1/f^2 intensity ratio observed between CeNi₂ and CeSb, and in preliminary measurements of other cerium compounds characterized by intermediate values of T_K , demonstrates that the in-

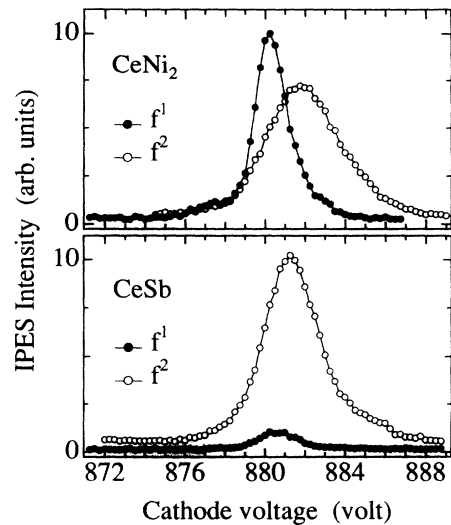


FIG. 3. Constant final state (CFS) curves for CeNi₂ (top) and CeSb (bottom). The curves are obtained by integrating, as a function of excitation energy, the RIPES signal within two energy windows (respectively 2.5 and 5 eV wide) that follow the position of the f^1 and the f^2 peaks.

tensity of the sharp f^1 resonance is a sensitive measure of configuration mixing in the initial state. The early measurements of γ -Ce of Ref. [15] also appear to follow this trend, although the occurrence of an $f^0 \rightarrow f^1$ resonance was not recognized at that time. The presence of a double resonance appears as a novel and general feature of the electron-addition spectral function of Ce materials. The material-dependent shape of the resonance reflects the configuration mixing in the ground state and sets independent constraints on the parameters of the Anderson Hamiltonian. Its description should therefore be considered as an important challenge for future theoretical work.

In conclusion, we have demonstrated in this Letter that the resonance occurring at the Ce $3d$ edge amplifies by roughly 2 orders of magnitude the conventional $4f$ bremsstrahlung cross section, so that this technique opens unprecedented possibilities to study valence fluctuations in Ce compounds. Resonant IPES offers for the investigation of the unoccupied states the same advantages as resonant PES for the occupied states. The site and symmetry selectivity is of crucial importance in many problems. Moreover, a number of investigations that are at present problematic or even impossible because of the inherently low signal level of IPES will become accessible with RIPES. Typical examples are detailed temperature-dependent studies of Ce materials [26], as well as surface or cluster studies, or even the use of dichroism. In perspective, we anticipate that RIPES will allow important progress in the investigation of the empty states in other correlated systems, like the uranium compounds. From the theoretical side, we hope that the present

demonstration of the power of this technique will motivate, beyond existing models [19,27], reliable calculations of the resonance profiles and of the energy-dependent spectral line shape, which are obvious prerequisites for the quantitative exploitation of this technique.

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