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Large Fermi-level resonance in the electron-addition spectrum of $CeRu_2$ and $CeIr_2$

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We report that the electron-addition spectra of superconducting $CeIr_2$ and $CeRu_2$, which are extreme examples of α-cerium-like behavior, display a very large peak of unresolved sharpness and position immediately above the Fermi level. We point out that such a peak is expected for a nonmagnetic system described by the Anderson Hamiltonian, and discuss its spectral weight and composition.

In this paper we report the room-temperature electron-addition spectra, as measured by bremsstrahlung isochromat spectroscopy (BIS), of $CeRu_2$ and $CeIr_2$, materials which exceed α-Ce in their extent of exhibiting collapsed volume and loss of magnetism, with $CeRu_2$ being the more extreme.[1] The two materials are also superconductors,[2] and $CeRu_2$ is again the more extreme with $T_c \sim 6$ K compared to the $T_c = 0.21$ K which we report here for $CeIr_2$. The BIS spectrum of both materials displays a very large peak of unresolved sharpness and position immediately above the Fermi level E_F. We point out below that such a peak is expected[3,4] for a nonmagnetic system described by the Anderson Hamiltonian, but we note that the data can also provide a test for other many-body[5–8] or single-particle[9,10] models of cerium $4f$ spectral weight.

The BIS study was motivated by our previous resonant photoemission study[11] of $CeRu_2$, which showed the cerium emission to be broadly peaked about 2.5 eV below E_F, and to be sharply rising again at E_F. Since its photon energy dependence in the resonance region is like that of peaks assigned to $4f$ emission in other cerium materials, the 2.5-eV peak was assigned as $4f$ emission, a very interesting finding in view of the traditional idea that the material's superconductivity implied tetravalent ($4f^0$) cerium. The resonance photon energy dependence of the E_F emission differs from that of the 2.5-eV feature in being shifted to lower photon energies by ~ 2 eV, which could occur for Ce $5d$ emission,[11] and so we regarded its assignment[12] as $4f$ emission to be an important issue deserving more experimental work. Because the BIS spectrum tends to be dominated by the large weight (14 for $4f^0$ and 13 for $4f^1$) for adding $4f$ electrons, there is now strong evidence from the large E_F BIS peak reported here that there is indeed a substantial $4f$ component in the E_F photoemission. But, as discussed below, some aspects of the spectral composition of this Fermi-level peak remain uncertain.

The BIS spectra were taken at a photon energy of 1486.6 eV using a factory-modified Vacuum Generators ESCALAB, operated under conditions yielding 0.5-eV resolution, as determined from a Ag Fermi-edge spectrum. Clean sample surfaces were obtained by fracturing polycrystalline ingots in a vacuum of 5×10^{-11} Torr. Valence-band and core-level x-ray photoemission was then measured, followed by BIS. During data taking, the chamber pressure was always below 7×10^{-11} Torr. BIS spectra were accumulated in sets of 25 sweeps and each set was compared to the first one taken for evidence of oxygen contamination. Room-temperature resonant photoemission spectra were obtained at the Stanford Synchrotron Radiation Laboratory as described in detail previously.[13] The $T_c = 0.21$ K of $CeIr_2$ was measured inductively at 16 Hz on a powdered sample in a He^3-He^4 dilution refrigerator, and had a 10% to 90% transition width of 0.15 K.

Figure 1 presents combined resonant photoemission and BIS data for $CeRu_2$ and $CeIr_2$. Combined spectra using these two techniques have not been reported previously for any material. For comparison and contrast, combined spectra are also shown for CeAl, an antiferromagnet ($T_N = 10$ K) with magnetic properties implying[13] a stable, unquenched cerium moment. For the former two compounds, the resonant photoemission spectrum is the difference of spectra taken with photon energies at the resonance maximum (122 eV) and before the resonance (115 eV), to show only the rise of emission due to the resonance at the cerium $4d$ edge. Such a difference spectrum, which discriminates against the strong emission from nearly filled Ru and Ir d states, is not necessary for CeAl. The details of the CeAl and $CeRu_2$ resonant photoemission spectra have been reported previously,[11,13] and for $CeIr_2$ it suffices here to note that the photon energy dependences for the emission at and below E_F differ just as in other cerium compounds.

For CeAl the spectral weight peaks about 2 eV below E_F and about 4 eV above E_F. The -2-eV feature has been assigned previously[13] as $4f^1 \rightarrow 4f^0$ emission, and the $+4$-eV feature has the asymmetric shouldered shape ascribed[14] to the $4f^2$ final-state multiplets of $4f^1 \rightarrow 4f^2$ transitions. Detailed analysis of the resonant photoemission data as described[15] by other workers yields a very small peak near E_F, but no peaking at E_F is evident in the raw data. Thus the spectrum is dominantly like that of the impurity Anderson Hamiltonian for an unquenched moment, with[13] a $4f$ binding energy $E_f \sim 2$ eV, a $4f$ width ~ 0.5 eV, and a Coulomb interaction $U \sim 6$ eV.

The $CeIr_2$ and $CeRu_2$ spectra contrast sharply with that of CeAl in having much weight around E_F. This weight is very asymmetric to energies just above E_F, with unresolved sharpness and position. However, there remains $4f^1 \rightarrow 4f^2$ weight near 5 eV, signaling that a large Coulomb interaction

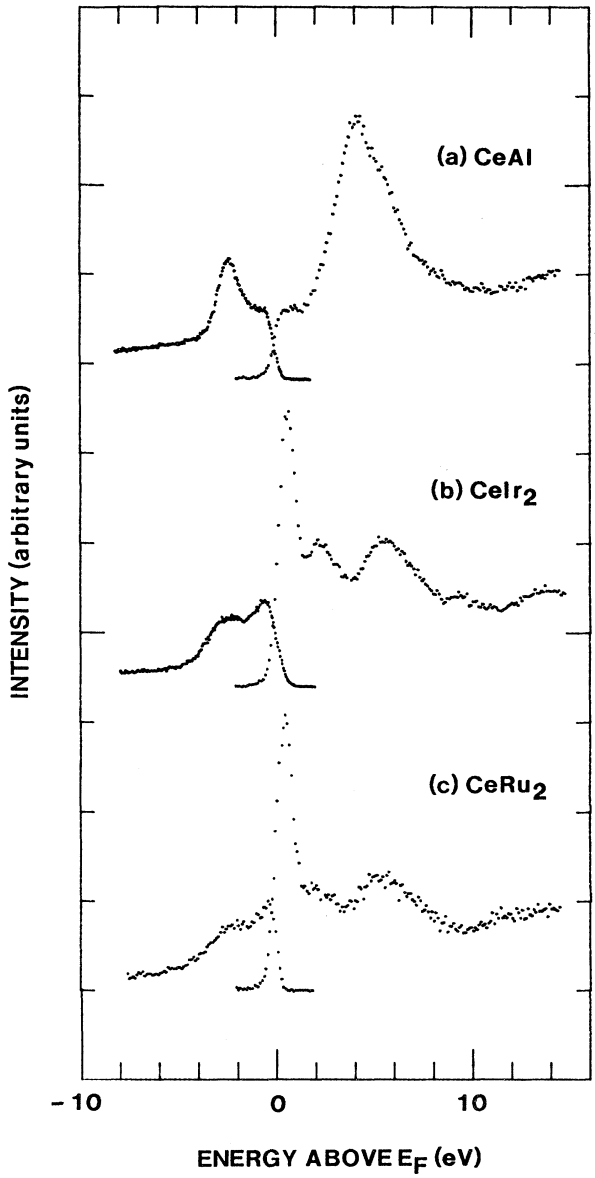

FIG. 1. Combined room-temperature resonant-photoemission and BIS spectra for (a) CeAl, (b) $CeIr_2$, and (c) $CeRu_2$. The photoemission resolution is 0.83 eV for (a) and (c) and 0.47 eV for (b). The BIS resolution is 0.5 eV. Other information is given in the text.

$U \sim 5$ eV persists. The $4f^1 \rightarrow 4f^2$ line shape is rather broad, probably due to $4f$ hybridization and $4f$ hopping, leaving an asymmetry to higher energy rather than a shoulder. The larger is the BIS E_F peak relative to the +5-eV peak, the larger is the photoemission E_F peak relative to the −2.5-eV peak, so it appears that the growth of weight at E_F is accomplished by a reduction of weight in the features further above and below E_F. With smaller magnitude, this effect was observed in resonant photoemission studies[15,16] of the cerium α-γ phase transition, and in the BIS spectrum[14] of $CePd_3$, but neither BIS nor combined spectra for α-Ce or extreme α-like materials have been reported. $CeIr_2$ and $CeRu_2$ also have smaller BIS peaks near +2 eV, which we tentatively attribute to Ir and Ru d weight displaced from below E_F by band-structure effects.

Both many-body and single-particle models of cerium $4f$ spectral weight have been proposed. We discuss below two models in which the implications for BIS spectra are reasonably clear. When other models[5–8] are extended quantitatively to the electron-addition spectrum it will be important to compare their predictions also with the BIS data presented above.

The Ce-Ce and Ce-Ru distances in $CeRu_2$ are very small and it has been proposed[12]that band theory can be applied directly to $CeRu_2$. Indeed, band calculations[17] for $CeRu_2$ and $CeIr_2$ reproduce several features of the spectra, the large $4f$ weight just above E_F and the spreading of $4f$ weight below E_F, due to both $4f$ hybridization and $4f$ hopping. However, the large $U \sim 5$ eV observed in the BIS spectrum shows clearly that the band-structure information cannot be applied directly without accounting for the effects of the Coulomb interaction, which suppresses ground-state charge fluctuations and expels $4f^1 \rightarrow 4f^2$ spectral weight to higher energies. In this sense it is possible that the 5-eV BIS peak is somewhat analogous[8] to the 6-eV photoemission peak in nickel materials, which shows such Coulomb effects on the broad nickel $3d$ bands, and is usually described using the Hubbard Hamiltonian with $U \sim 2$ eV.[18] However, a direct analogy to ferromagnetic nickel leaves it unclear why the much larger cerium U value does not stabilize a magnetic ground state.

A description which includes the large U value and emphasizes conduction-electron compensation of the cerium moments through $4f$-band hybridization is provided[3] by the Anderson Hamiltonian. For either the impurity[19] or lattice[4] cases, arguments based on the Friedel or Luttinger sum rules show that for a nonmagnetic system an E_F peak is expected even though the energetics of the $4f$ binding energy and the large-U value also require considerable weight well above and well below E_F. For temperatures less than the characteristic spin fluctuation energy E_K, a condition satisfied at room temperature for $CeIr_2$ and $CeRu_2$, this leads to a three-peaked spectrum[20] where the central E_F feature is expected to be sharper than the two other peaks and to have increasing spectral weight as E_K increases. These are exactly the general features of the observed spectra, if the evolution of α-like properties is interpreted as an increase in E_K, a picture which is semiquantitatively successful for relating photoemission data to magnetic properties in some cerium materials,[13,21,22], and for describing the thermodynamics of the α-γ transition.[23,24]

A Fermi-level peak approximately satisfying the Friedel sum rule has been derived[25] recently by Gunnarsson and Schönhammer (GS) for an Anderson impurity model with large orbital degeneracy, as is appropriate for cerium. Using this model GS (Ref. 26) have obtained reasonable fits of the Ce $3d$ and valence-band emission of $CeRu_2$. The GS theory can also be applied[27] to the areas A_0 and A_1 of the E_F and 5-eV BIS peaks to deduce the fraction ξ_0 of $4f^0$. In this theory, the E_F peak is largely $4f^0 \leftrightarrows 4f^1$ weight, but there is also some configuration-interaction mixing of the $4f^0 \rightarrow 4f^1$ and $4f^1 \rightarrow 4f^2$ weights. Taking simple straight-line backgrounds under the peaks leads to $2 < (A_0/A_1) < 3$, for which the GS theory[27] gives $0.44 < \xi_0 < 0.5$. This value of ξ_0 is a factor ~ 2 larger than the $\xi_0 \sim 0.2$ to 0.25 de-

duced from core-level photoemission or photoabsorption spectra[26,28] and a more sophisticated background treatment does not remove the problem. Further, current theoretical understanding[26,29] makes it impossible to attribute such a large difference to final-state configuration-interaction effects in the core-level spectra, because in these spectra the separation of the $4f^0$ peak from the $4f^1$ and $4f^2$ peaks is very large, ~ 10 eV, compared to reasonable values of the hybridization matirx element $\lesssim 2$ eV.

This discrepancy with the BIS weight of the E_F peak and the unexplained resonance-photon-energy dependence of its photoemission part is motivation to consider the effects of the $4f$ hopping found in band calculations but omitted from the Anderson Hamiltonian. As mentioned previously,[21] it seems likely that a tendency toward $4f$ banding would increase the fraction of ground state $4f^2$ so that the E_F peak would contain more $4f^1 \leftrightarrows 4f^2$ weight than for the Anderson model, which would reduce the value of ξ_0 deduced above. In the photoemission part of the peak, the presence of $4f^2 \rightarrow 4f^1$ weight could provide an explanation of the resonance photon energy dependence since studies[30] of mixed valent systems have shown that the photon energy of the $f^n \rightarrow f^{n-1}$ resonance is shifted by ~ 1 to 2 eV relative to that of $f^{n-1} \rightarrow f^{n-2}$. Finally, due to compensation of $4f^0$ by $4f^2$ in the ground state, the total number of $4f$ electrons would be maintained closer to or in excess of 1, as found in Compton scattering[31] on α-Ce and in density-functional calculations for cerium[9] and its compounds.[10,17]

In summary, combining BIS spectra with resonant photoemission spectra for an extreme γ-like and two extreme α-like cerium materials reveals unambiguously a very large growth of spectral weight around the Fermi level, which increases as the extent of α-like properties increases. We have pointed out that band models require qualitative modification to include the large Coulomb interaction seen in the spectra, but that there remain quantitative uncertainties concerning the spectral weight and composition of the E_F peak in current Anderson Hamiltonian models.

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