

## CeRu<sub>2</sub> and CeCo<sub>2</sub>: Superconductors with 4*f* electrons

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CeRu<sub>2</sub> and CeCo<sub>2</sub> have been considered to have tetravalent Ce because of their superconductivity, collapsed volume, and lack of magnetic moments. Resonant photoemission studies show these compounds to be mixed valent, suggesting the need to reexamine the mechanism of their superconductivity.

CeRu<sub>2</sub> and CeCo<sub>2</sub> are superconductors with transition temperatures  $T_c$  of 6 and 1 K, respectively.<sup>1,2</sup> It has generally been assumed that Ce in these materials is tetravalent, i.e., 4*f*<sup>0</sup>, because studies in which Ce is introduced into various superconducting matrices have shown that a localized 4*f* electron, either magnetic or nonmagnetic, drives the host  $T_c$  to zero for only a few atomic percent Ce.<sup>3</sup> CeRu<sub>2</sub> and CeCo<sub>2</sub> also display collapsed volume and a loss of magnetic moments, properties which are common to a group of Ce intermetallic compounds and which are often taken to signal tetravalent Ce for the group.<sup>4</sup> Alternatively, mixed valence has been proposed for various of these compounds,<sup>5,6</sup> and, based on a reexamination of the cerium atomic volume and on their 2*p* core-level absorption spectra, there is a recent contention that no intermetallic tetravalent cerium compounds exist.<sup>7,8</sup> This severely challenges the traditional understanding of superconductivity in CeRu<sub>2</sub> and CeCo<sub>2</sub>, especially since superconductivity has been reported for only one other material known with certainty to be mixed valent, CeCu<sub>2</sub>Si<sub>2</sub>, for which the  $T_c$  of ~0.5 K is less than a tenth that of CeRu<sub>2</sub>.<sup>9,10</sup>

This Communication describes the results of resonant photoemission measurements on CeRu<sub>2</sub> and CeCo<sub>2</sub>, made to search for 4*f* emission. It is convenient to compare with a material known to have 4*f* electrons, and therefore data are also presented for CeAl<sub>3</sub>, which is interesting in its own right because it displays 4*f* electron demagnetization below ~5 K.

The photoemission experiments reported here were performed at the Stanford Synchrotron Radiation Laboratory using equipment, operating conditions, and experimental procedures exactly as described previ-

ously.<sup>11</sup> The samples were polycrystalline ingots, fractured *in situ* in a vacuum of  $1 \times 10^{-10}$  Torr, and superconductivity with the correct  $T_c$  was verified for the samples of CeRu<sub>2</sub> and CeCo<sub>2</sub>. Figures 1, 2, and 3 show the valence-band photoemission spectra of CeAl<sub>3</sub>, CeRu<sub>2</sub>, and CeCo<sub>2</sub>, respectively, for several photon energies  $h\nu$  between 80 and 130 eV.

The interpretation of resonant photoemission data for any cerium material, and especially one believed to have no 4*f* electrons, must take account of the

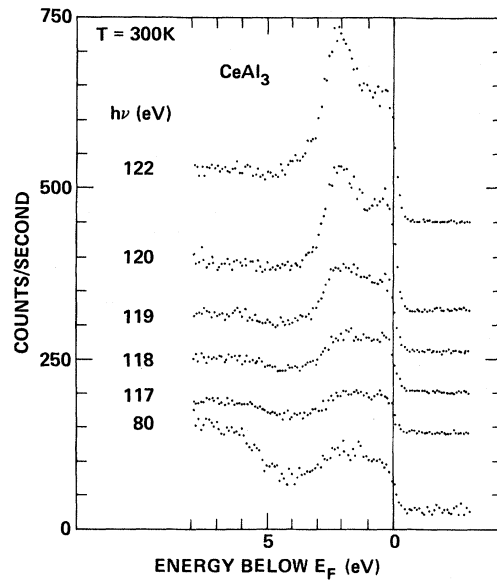


FIG. 1. CeAl<sub>3</sub> valence-band photoemission spectra for several photon energies. The resolution varies from 0.41 eV at 80 eV to 0.47 eV at 122 eV.

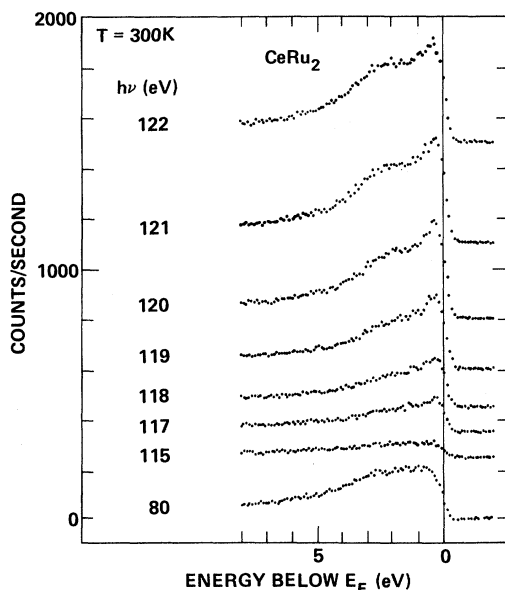


FIG. 2.  $\text{CeRu}_2$  valence-band photoemission spectra for several photon energies. The resolution varies from 0.41 eV at 80 eV to 0.47 eV at 122 eV.

fact that the Ce  $5d$  emission resonates with multiplicative gain as large as 0.5 that of the  $4f$  electrons. That this is so is known experimentally from studies of Gd and Tm, where the  $4f$  and  $5d$  emission do not overlap.<sup>12,13</sup> It is therefore necessary to have a spectroscopic criterion to identify  $4f$  emission. In  $\text{CeAl}_3$ , as

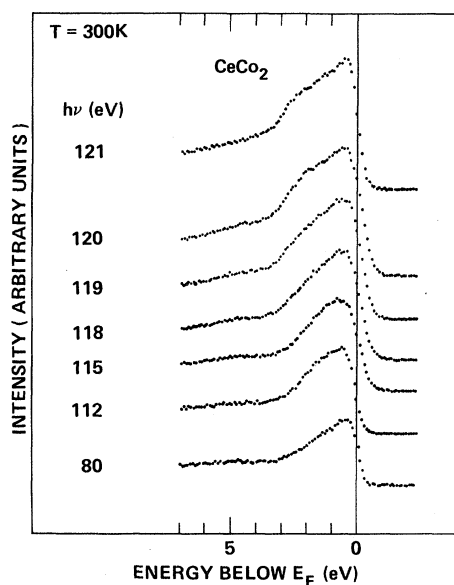


FIG. 3.  $\text{CeCo}_2$  valence-band photoemission spectra for several photon energies. The resolution is 0.83 eV for the 115–120-eV spectra, and is 0.41, 0.45, and 0.46 eV for the 80-, 112-, and 121-eV spectra, respectively.

in cerium itself and many other compounds, the most prominent feature in the on-resonance spectrum (photon energy  $h\nu = 121\text{--}122$  eV) occurs at  $\sim 2$ -eV binding energy and all workers who have made resonant photoemission studies of cerium compounds agree that this peak has  $4f$  origin.<sup>11,14–16</sup> An identifying feature of its resonance behavior is that this peak becomes predominant only for  $h\nu > 118$  eV, although the entire valence band resonates for  $h\nu > \sim 112$  eV, the Fano minimum.

For the spectra of  $\text{CeCo}_2$  and  $\text{CeRu}_2$  the broad emission at  $\sim 2.6$ -eV binding energy behaves in exactly the same fashion and is therefore assigned as  $4f$  emission. Although in these cases the  $4f$  state is more difficult to pick out because it is broad and located on a large background of Co or Ru  $d$  states, the similarity to the behavior in  $\text{CeAl}_3$  is unmistakable. The finding of  $4f$  emission in  $\text{CeRu}_2$  and  $\text{CeCo}_2$ , and its greater width than in  $\text{CeAl}_3$ , is qualitatively consistent<sup>17</sup> with all reported core-level photoemission and photoabsorption spectra, which show both  $4f^0$  and  $4f^1$  structure for  $\text{CeCo}_2$  (Refs. 8 and 18) and  $\text{CeRu}_2$ ,<sup>19</sup> but only  $4f^1$  structure for  $\text{CeAl}_3$ .<sup>20</sup>

There is not complete agreement about the assignment of the resonating emission nearer to the Fermi level in Ce valence-band photoemission. Some workers<sup>11</sup> assign it as  $5d$  emission, and this assignment is supported by the fact that strongly resonating  $5d$  emission is expected in the spectrum,<sup>12,13</sup> and by the behavior pointed out above, that its resonance begins and peaks at slightly lower photon energies than for the 2-eV feature. Such a difference for  $n = 4$  and 5 shell emission was predicted theoretically<sup>21</sup> and observed experimentally<sup>22</sup> for the  $4d$ ,  $5s$ ,  $5p$ , and  $5d$  lanthanum emission of  $\text{LaB}_6$ . Other workers<sup>23–25</sup> have asserted that, in some cerium materials, the emission near the Fermi level is also of  $4f$  origin. Based on previous work, then, the sharp feature near  $E_F$  in the  $\text{CeRu}_2$  spectrum could be assigned either as  $4f$  or  $5d$ . We prefer the  $5d$  assignment for the reasons given above, but at present this is an unresolved issue.

Since the resonance technique has been used here to identify  $4f$  emission well away from the Fermi level, it should be mentioned that Baer and his collaborators<sup>20</sup> have given a number of arguments that in several cerium materials, including  $\gamma$ -Ce and  $\text{CeAl}_3$ , the  $4f$  emission lies very close to the Fermi level, with the remainder of the spectrum being of  $5d$  origin. Of necessity these arguments are all indirect, having been undertaken to overcome the fact that the small spectral weight and lack of spectral structure of the  $4f^1 \rightarrow 4f^0$  transition have made it impossible to identify by direct spectroscopic means in conventional x-ray photoemission (XPS). Other XPS workers<sup>26,27</sup> have also confronted this problem and have found cause to place the  $4f$  emission at 2 eV in  $\gamma$ -Ce, in agreement with the conclusions from resonant photoemission.

Considering now these materials' superconductivity, at present we can only point out certain relevant aspects of the problem. Translational symmetry is the most obvious new ingredient capable of superceding the impurity behavior described in the opening paragraph, because it implies coherent  $4f$  states with vanishing quasiparticle scattering as  $T \rightarrow 0$ . The details of the  $4f$  coherence have yet to be elucidated. Although a simple  $4f$  band model could account for the rather temperature-independent magnetic susceptibilities<sup>2</sup> of  $\text{CeCo}_2$  and  $\text{CeRu}_2$ , such a model is inappropriate if the  $4f$  Coulomb energy  $U$  is  $\sim 5\text{--}6$  eV, as claimed from Bremsstrahlung isochromat spectroscopy on several cerium materials.<sup>20</sup> Presumably some sort of Fermi-liquid picture applies at low temperature and  $T_c$  is then material dependent, being governed by the quasiparticles' residual interactions, about which little is known, and by their coupling to phonons, possibly strong in a mixed valent system. As has been emphasized for  $\text{CeCu}_2\text{Si}_2$  (Ref. 9) a Fermi-liquid enhancement of  $\gamma$  may be important; the values of  $\gamma$  for  $\text{CeRu}_2$  and the isostructural  $4f^0$  compound  $\text{LaRu}_2$  are,<sup>28</sup> respectively,  $23.3 \pm 0.61$  and

$13.6 \pm 0.13$  mJ/mole  $\text{K}^2$ , in roughly the same ratio as the values of  $T_c$ , which are 5.92 and 3.2 K, respectively. The Debye temperatures of  $\text{CeRu}_2$  and  $\text{LaRu}_2$  are nearly equal, implying similar phonon spectra, although the possibility is not ruled out that a particular feature of the phonon spectrum may account for the higher  $T_c$  of  $\text{CeRu}_2$ . Finally, the fact that rare-earth substitutions in  $\text{CeRu}_2$  initially raise  $T_c$ , even when the rare-earth ions carry localized moments,<sup>1</sup> is motivation to speculate that the response of the cerium lattice Fermi liquid to magnetic impurities is different than that of other Fermi liquids.

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