Crystal electric fields in heavy-electron metals: The specific heats of U$_2$Zn$_{17}$ and CeCu$_6$ to 70 K

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Two temperature scales—(1) $T_0$ (single impurity) and/or $T_F^*$ (degenerate Fermi) and (2) crystal-electric-field splitting(s) $\Delta$—provide the basis for dividing the excitation spectra of heavy-electron systems into three regimes. They are (i) for $T_0 < T < \Delta$, the specific heat and susceptibility are that due to independent $f$ atoms in a crystal field; (ii) for $T \sim T_0$, a bump appears in the specific heat due to the Kondo compensation; (iii) for $T < T_0$, interaction effects between the $f$ atoms lead to a Fermi-liquid solid where band-structure effects show up in the low-temperature properties ($T < T_F^*/100$). This paper is primarily concerned with region (i). In particular, we present new specific-heat data for U$_2$Zn$_{17}$ up to 70 K and CeCu$_6$ to 80 K. In comparing these data with those for other heavy-electron materials we conclude that the specific heat for $T > T_0$ is qualitatively consistent with the existence of crystal-electric-field levels, but that the overall experimental entropy is too high. We present a tentative model to account for this discrepancy through the use of Fermi statistics to describe transitions in a stylized band model with two peaks. Crystal-field levels in most cases have not been confirmed by neutron scattering.

I. INTRODUCTION

Heavy-fermion materials are usually identified by their striking behavior at very low temperatures. The linear coefficient of specific heat and the low-temperature susceptibility indicate a huge effective mass; the resistivity bends over and tends toward zero, signaling coherence effects. However, unusual and distinctive features are also seen in these materials at higher temperatures. For example, even the conventionally dull specific heat shows structure at temperatures as high as 100 K. Structure at various temperature scales is also seen in other, nonequilibrium properties—thermopower and magnetoresistance are good examples. In this paper we concentrate on the specific heat.

Since heavy-fermion materials are rare-earth and actinide-element compounds, an obvious first scale is the single-impurity Kondo temperature. However, even a Kondo peak scaled to lattice concentrations does not fully explain the data. Rare earths, and Ce in particular, are well known to exhibit crystal-electric-field (CEF) effects. Experiments are now beginning to see CEF levels in uranium compounds as well. As a start at understanding energy scales in these materials, it seems reasonable to investigate theoretically the effect CEF will have on, for example, the static equilibrium properties. One must note, however, that without neutron scattering experiments it is often difficult to directly extract the existence, let alone the level spacings, of CEF levels from equilibrium measurements.

Specific-heat measurements are a more sensitive probe of crystal-electric-field levels than susceptibility measurements. The reason can be seen by contrasting these two quantities for a simple two-level system with the lower level having a degeneracy $g_1$ and effective magnetic moment $p_1$ (in units of $\mu_B$) and the upper level, lying $\Delta$ above the lower, with degeneracy $g_2 = g_1 g_r$ ($g_r$ is the relative degeneracy) and moment $p_2$. The specific heat ($\beta=1/k_B T$)

$$C = \frac{g_r (\beta \Delta)^2 \exp(-\beta \Delta)}{[1 + g_r \exp(-\beta \Delta)]^2}$$

has a maximum at $\beta \Delta \sim 2$, while the susceptibility

$$\chi = \left| \frac{\mu_B^2}{3k_B T} \right| \frac{p_1^2 + \Delta^2 + 3g_r \exp(-\beta \Delta)}{1 + g_r \exp(-\beta \Delta)}$$

only deviates slightly from the otherwise expected Curie-law behavior. Combination of both measurements can permit the identification of the levels, their degeneracies, and effective moments, data which could also be obtained by more precise but also more difficult neutron-scattering measurements.

Crystal-electric-field levels are more usually of interest for magnetic ions in insulators than in metals where the contributions of the conduction electrons (and phonons for the specific heat) typically dominate the equilibrium properties. However, the partially filled $f$-electron states in the rare earths and actinides are so localized that the CEF splittings are small enough ($\Delta \sim 100$ K) [compared
to the transition metals where the CEF splittings of the $d$ electrons exceed 1000 K] that they can be detected by specific-heat measurements. There is extensive literature\textsuperscript{1,2} for the levels of these atoms as impurities in insulators, but very little concerning the levels for such impurities in metals. In addition, there is almost no experimental evidence for U CEF levels in metallic compounds, whereas there is evidence for Ce CEF levels (cf. Table IV for references). In fact, this paper offers one of the first examples of crystal-electric-field-like levels in U$_2$Zn$_{17}$ (see Sec. IV). We note also that CEF levels have been reported in UBe$_{13}$\textsuperscript{3}.

An essential difficulty in detecting CEF levels in metals is the presence of a large lattice contribution to the specific heat, in addition to that from the conduction electrons. Accordingly, it is always necessary to subtract the specific heat of an isostructural compound having no $f$ electrons and similar lattice constant. For example, we use data for Th$_2$Zn$_{17}$ to approximate the lattice contribution in U$_2$Zn$_{17}$. In addition, Th$_2$Zn$_{17}$ is a metal, so in the calculation of $\Delta C(T)$ which is done on a per mole basis,

$$\Delta C = C(\text{U}_2\text{Zn}_{17}) - C(\text{Th}_2\text{Zn}_{17}),$$

we are necessarily removing some of the conduction-electron contribution. If we could be sure that the number of non-$f$-electrons were the same in the heavy-electron and comparison compounds (as might be the case if U has a $f^2$ configuration), then the resulting $\Delta C(T)$ would contain essentially only contributions from the $f$ electrons. But given that any heavy-electron compound contains admixtures of at least two valences and that, furthermore, the conduction electrons are hybridized with the $f$ electrons, we know that $\Delta C(T)$ must contain, besides the $f$-electron contribution, some positive residue of the conduction electrons. Still we suppose that this residue has the weak electronic contribution expected of ordinary metals.\textsuperscript{4} Accordingly, we can integrate $\Delta C(T)$ to extract the entropy difference $\Delta S(T)$ due to the $f$ electrons,

$$\Delta S(T) = \int_0^T \frac{\Delta C(T')}{T'} dt'.$$

This $\Delta S(T)$ is thus a measure of the number of degrees of freedom per $f$ atom [$n_{\text{dof}}(T)$], according to the relation

$$\Delta S(T) / R = \ln(n_{\text{dof}}(T)).$$

As we shall see the deduced $n_{\text{dof}}(T)$ is consistent with a CEF model for Ce compounds, but leads to a serious inconsistency in the case of U$_2$Zn$_{17}$.

In order to identify the features of the specific heat, models are needed. To start, we include the obvious effects first, and then consider possible refinements. In the case of heavy fermions, these “obvious” effects are single-impurity Kondo behavior, coherence effects beginning at the effective degeneracy temperature, and crystal-field effects. The plan of the paper is as follows. Section II describes a “standard model” for the excitations of heavy-electron metals with emphasis on relevant energy scales. The experimental methods are described in Sec. III, and results for U$_2$Zn$_{17}$ and CeCu$_6$ are presented in Sec. IV. Section V contains discussion of these results, with reference to the “standard model” of Sec. II. Conclusions appear in Sec. VI.

II. “STANDARD MODEL” FOR EXCITATIONS IN HEAVY-ELECTRON METALS

In the absence of any comprehensive theory for heavy-electron metals, a series of models has evolved to cover various temperature ranges. Here we attempt to combine the various points of view into a “standard model” which will serve as a basis both for summarizing the data and for discussing flaws in the model itself. At the outset we stress that the “standard model” has developed in response to the data for Ce compounds. There is little evidence for its applicability in U compounds; in fact, one aim of this paper is to stimulate more high- (and low-) temperature measurements on U systems.

Roughly speaking there are two important temperatures: $T_0$ characterizing the single-impurity behavior and $T_F$ characterizing the very-low-temperature “coherent” behavior. Table I lists these temperatures, together with the effective masses that can be associated with the low-temperature specific heat. The characteristic numbers are deduced in the following ways.

$T_0$: The inverse of the high-temperature magnetic susceptibility versus temperature has the following interpolation formulas for spin $S = \frac{1}{2}$:

$$\chi^{-1}(T) \propto T + 1.82 T_0 \quad \text{for} \quad 0.6 T_0 < T < 20 T_0.$$

Since the bulk of the ground state levels are doublings (only CeB$_6$ is believed to have a quartet ground state) and the crystal-field splitting usually exceeds $T_0$, this formula is a reasonable guide to $T_0$. In Table I the negative temperature intercept of $\chi^{-1}(T)$ is taken to be $2 T_0$ for simplicity.

$T_F$: At temperatures far below the effective degeneracy temperature $k_B T_F = \langle \hbar k_F \rangle^2 / (2m^*)$, $C(T)/T$ approaches the zero-temperature specific-heat coefficient $\gamma(0) = m^* k_F^2 / 3 \pi^2$ where the value of $k_F$ is deduced via $n = k_F^3 / 3 \pi^2$. In Table I we assume that both Ce and U have one conduction electron. [Since $T_F \propto n / \gamma(0)$ other choices for $n$ can easily be translated into $T_F$.]

To date, there is no theoretical connection between $T_0$ and $T_F$, nor does Table I suggest one. There are at least two problems connected with deducing $T_0$, under the assumption that the single-impurity susceptibility is valid for the concentrated system. First, there is always the possibility that there may be yet another energy scale associated with the RKKY interactions between U atoms, denoted by $I_{\text{RKKY}}$. The reliability of the formula above for the inverse susceptibility will then depend on $I_{\text{RKKY}}$ being much less than $T_0$. One way of judging whether or not we are in this limit (i.e., $I_{\text{RKKY}} \ll T_0$) is by comparing the antiferromagnetic transition temperatures ($T_N \sim I_{\text{RKKY}}$) with $T_0$. Tables I and II suggest that the Néel temperature $T_N$ is generally smaller than $T_0$ for Ce compounds and generally larger than $T_0$ for U compounds.
TABLE I. Single-impurity temperature $T_0$ and effective degeneracy temperature $T_F^*$ for some heavy-electron metals. See discussion in the text (Sec. II) for methods used to extract $T_0$ from the high-temperature susceptibility and $T_F^*$ from the specific-heat coefficient $\gamma(T) = C(T)/T$ "extrapolated" to zero temperature. Note that $T_0$ may be larger or smaller than $T_F^*$. All $T_0$ are deduced from the $\chi(T)$ data in Ref. 41 unless otherwise indicated. All $T_F^*$ and $m^*/m$ values are from Ref. 42; the source of the $\gamma(0)$ value used in the calculation is cited.

<table>
<thead>
<tr>
<th>Crystal structure</th>
<th>Symmetry</th>
<th>Ce compound (typical examples)</th>
<th>$T_0$ (K)</th>
<th>$T_F^*$ (K)</th>
<th>$m^*/m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>cubic</td>
<td>CeAl$_3$</td>
<td>20</td>
<td>34</td>
<td>440</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CeCu$_2$Si$_3$</td>
<td>60</td>
<td>41</td>
<td>540</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CeCu$_6$</td>
<td>20</td>
<td>28</td>
<td>670</td>
</tr>
<tr>
<td></td>
<td></td>
<td>UBe$_{13}$</td>
<td>35$^b$</td>
<td>37$^b$</td>
<td>430</td>
</tr>
<tr>
<td></td>
<td></td>
<td>UP$_{13}$</td>
<td>&gt;25$^c$</td>
<td>91$^t$</td>
<td>270</td>
</tr>
<tr>
<td></td>
<td></td>
<td>U$<em>2$Zn$</em>{17}$</td>
<td>&lt;65$^d$</td>
<td>50$^g$</td>
<td>300</td>
</tr>
</tbody>
</table>

$^a$Reference 45.
$^b$Reference 46.
$^c$Reference 47.
$^d$Reference 48.
$^e$Reference 19.
$^f$Reference 49.
$^g$Reference 20.
$^h$Reference 50.
$^i$Reference 51.

The second possible problem is that the value of $T_0$ deduced from the inverse susceptibility may be influenced by the presence of a comparable CEF level. In the one case for which relevant data exists we can clearly illustrate this. The high-temperature inverse susceptibility for Ce$_x$La$_{1-x}$B$_6$ (per mole of Ce) has the concentration-independent value of $T_0=50$ K. On the other hand, at low concentrations of Ce the low-temperature inverse susceptibility yields $T_0 \sim 1$ K. We know that there is a crystal-field splitting of 500 K between the low-lying quartet and the doublet. So we expect that this splitting has worked to produce a higher value of $T_0$. In addition we cannot discount that the RKKY and other interactions between the Ce atoms have raised the low $T_0$ (1 K) for the dilute system to a higher value in the concentrated one.

Given that $T_0$ and $T_F^*$ are comparable, the simplest procedure is to consider temperature scales that are large compared to $T_0$, comparable to $T_F^*$, and small compared to $T_0$ and $T_F^*$. These three regimes characterize the "standard model" summarized in Table III.

**Single-impurity regime.** ($T > T_0$). The susceptibility

TABLE II. Antiferromagnetic transition temperatures $T_N$ for Ce compounds (Ref. 43) and U compounds (Ref. 44), arranged by crystal structure of decreasing symmetry.

<table>
<thead>
<tr>
<th>Crystal structure</th>
<th>Symmetry</th>
<th>Ce compound (typical examples)</th>
<th>$T_N$ (K)</th>
<th>U compound (typical examples)</th>
<th>$T_N$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>cubic</td>
<td>CeMg</td>
<td>18–20</td>
<td>UN</td>
<td>52</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CeZn</td>
<td>29–36</td>
<td>UP</td>
<td>125</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CeAl$_2$</td>
<td>4–4.6</td>
<td>UAs</td>
<td>127</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CeP$_{13}$</td>
<td>1.6</td>
<td>UIn$_2$</td>
<td>260</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CeIn$_3$</td>
<td>11</td>
<td>UIn$_3$</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CeTi$_1$</td>
<td>no</td>
<td>UGa$_3$</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CePb$_1$</td>
<td>no</td>
<td>UTi$_1$</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CeCu</td>
<td>2.7</td>
<td>UPb$_1$</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>orth</td>
<td>CeGe</td>
<td>10</td>
<td>U$<em>2$Zn$</em>{17}$</td>
<td>15</td>
</tr>
<tr>
<td>BaCd$_{11}$</td>
<td>orth</td>
<td>CeZn$_2$</td>
<td>7</td>
<td>UCD$_{11}$</td>
<td>10</td>
</tr>
<tr>
<td>Th$<em>2$Zn$</em>{17}$</td>
<td></td>
<td>CeCd$_{11}$</td>
<td>no</td>
<td>U$<em>2$Zn$</em>{17}$</td>
<td>10</td>
</tr>
</tbody>
</table>

$^a$Reference 41.
$^b$Reference 41.
TABLE III. Description of the standard model for the excitations in a heavy-electron metal in terms of the temperature ranges, nature of the excitation, form of the specific heat, and typical examples.

<table>
<thead>
<tr>
<th>Temperature range</th>
<th>Nature of excitations</th>
<th>Expected specific heat</th>
<th>Typical examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_0 &lt; T &lt; \Delta$</td>
<td>$f$ atoms interacting with conduction electrons and CEF levels</td>
<td>Peaks in $\Delta C(T)$</td>
<td>CeAl$_3$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$T_{\text{peak}} \sim \Delta/2.4$</td>
<td>CeCu$_2$Si$_2$</td>
</tr>
<tr>
<td>$T \sim T_0$</td>
<td>Conduction electrons Kondo screen $f$-atom spin</td>
<td>Peak in $\Delta C(T)$</td>
<td>CeAl$_3$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$T_{\text{peak}} \sim T_0$</td>
<td></td>
</tr>
<tr>
<td>$T \ll T_p^*, T_0$</td>
<td>Fermi liquid with band structure</td>
<td>Low-temperature structure in properties</td>
<td>CeAl$_3$</td>
</tr>
</tbody>
</table>

is well explained as the sum of susceptibilities for single $f$ atoms, each interacting only with the conduction electrons. As the temperature decreases, $\chi(T)$ changes from a Curie law to the interporation formula used to deduce $T_0$ due to interactions with the conduction electrons. At still lower temperatures the impurity spin ($S = \frac{1}{2}$ usually assumed in theories) would be completely screened by the conduction electrons, if interactions effects in concentrated systems did not affect the susceptibility.

For $T > T_0$, the specific heat should be that of independent $f$ atoms—i.e., we expect to see the effect of the crystal-field levels as peaks in the specific heat. The position of the peak $T_{\text{peak}}$ can be used to estimate the crystal-electric-field splitting $\Delta$ according to $\Delta = (\text{prefactor})T_{\text{peak}}$; the prefactor 2.4 is only weakly dependent on the relative degeneracy. (For example, for Ce with $J = \frac{1}{2}$ in a cubic field, the prefactor is 2.23 if the quartet is lower and 2.65 if the doublet is lower. For U this factor can be as large as 3.0 if two quartets lie above the ground-state doublet.)

This simple-minded approach works best for CeAl$_3$ (see Table IV) where the CEF splitting is roughly twice the temperature of the peak in the electronic specific heat. However, even in this case there is difficulty with

TABLE IV. Electronic entropy and temperature of electronic specific-heat maximum, with comparison of the smallest measured crystal-electric-field splitting, for the heaviest heavy-electron compounds. With two exceptions only those compounds are listed for which a comparison compound is available. If the peak in $\Delta C(T)$ can be interpreted as a Schottky anomaly then, assuming only doublet levels, the smallest CEF splitting should be $\sim 2.4T_{\text{peak}}$.

<table>
<thead>
<tr>
<th>Heavy-electron compound</th>
<th>Comparison compound</th>
<th>$\Delta S/R$ at stated temperature</th>
<th>Temperature of $\Delta C$ peak (K)</th>
<th>Smallest CEF splitting (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeAl$_3$</td>
<td>LaAl$_3$</td>
<td>$\Delta S/R &lt; 15$ at 200 K$^a$</td>
<td>30$^g$</td>
<td>60$^g$</td>
</tr>
<tr>
<td>CeAl$_2$</td>
<td>LaAl$_3$</td>
<td>$\Delta S/R &lt; 15$ at 200 K$^c$</td>
<td>40$^g$</td>
<td>100$^4$</td>
</tr>
<tr>
<td>CeCu$_2$Si$_2$</td>
<td>LaCu$_6$</td>
<td>$\Delta S/R &lt; 15$ at 400 K$^e,f$</td>
<td>150$^g$</td>
<td>863$^a$</td>
</tr>
<tr>
<td>CeRu$_2$Si$_2$</td>
<td>LaRu$_2$Si$_2$</td>
<td>$\Delta S/R &lt; 15$ at 100 K$^h$</td>
<td>27$^l$</td>
<td></td>
</tr>
<tr>
<td>CeCu$_6$</td>
<td>LaCu$_6$</td>
<td>$\Delta S/R &lt; 15$ at 70 K$^i$</td>
<td>26$^l$</td>
<td></td>
</tr>
<tr>
<td>CeB$_6$</td>
<td>LaB$_6$</td>
<td>$\Delta S/R &lt; 15$ at 300 K$^l$</td>
<td>530$^{m}$</td>
<td></td>
</tr>
<tr>
<td>UBe$_{13}$</td>
<td>ThBe$_{13}$</td>
<td>$\Delta S/R &lt; 15$ at 10 K$^n$</td>
<td>3$^p$</td>
<td>180$^{n,p}$</td>
</tr>
<tr>
<td>U$<em>2$Zn$</em>{17}$</td>
<td>Th$<em>2$Zn$</em>{17}$</td>
<td>$\Delta S/R &lt; 15$ at 10 K$^o$</td>
<td>70$^p$</td>
<td></td>
</tr>
<tr>
<td>UCd$_{13}$</td>
<td>none</td>
<td>$\Delta S/R &lt; 15$ at 10 K$^u$</td>
<td>$\sim 50^a$</td>
<td>not seen$^l$</td>
</tr>
</tbody>
</table>

$^a$Reference 35.
$^b$Reference 10.
$^c$Reference 52.
$^d$Reference 53.
$^e$Reference 36.
$^f$Reference 54.
$^g$Reference 35.
$^h$Reference 55.
$^i$Reference 56.
$^j$Reference 20.
$^k$Reference 57.
$^l$This work.

$^m$Reference 58.
$^n$Reference 59.
$^o$Reference 60.
$^p$Reference 3.
$^q$Reference 61.
$^r$Reference 62.
$^s$Reference 63.
$^t$Reference 64.
$^u$Reference 34.
$^v$Reference 63.
this interpretation. In particular, the specific-heat peak, supposedly due to a CEF, is smaller in magnitude and wider in temperature than predicted.

In contrast, for CeCu$_2$Si$_2$ the peak is not connected with any known CEF level splitting. Furthermore, in this case the measured peak is larger in magnitude and narrower than a CEF level would predict, i.e., just the reverse of CeAl$_3$. We will return to the problem of detecting CEF levels from the specific heat after discussing the new data presented in Sec. IV.

"Kondo regime" ($T \sim T_0$). For temperatures comparable to the single-impurity temperature $T_0$, the conduction electrons screen the impurity spin associated with the lowest CEF level. From the theoretical work on the single-impurity problem, we know that in the $f$-projected density of states there is a peak at $\sim T_0$ above the Fermi level. This peak, which is temperature dependent, gives rise to a peak in the specific heat at $T \sim T_0$. Such peaks have been seen in many dilute-impurity systems and may also be present in heavy-electron materials.

The effects of crystal fields on the Kondo-based peak of the specific heat have been studied by Desgranges and Rasul for the cases of two doublets and three doublets (equally spaced). As the CEF increases, splitting a fourfold level into two doublets, a shoulder develops in the specific heat, and eventually two peaks form on either side of the original fourfold level. The lower peak can be associated with the Kondo effect involving the low-lying doublet, and the upper with a Schottky anomaly. They obtain similar results for the sixfold case splitting into three doublets.

The main features of the resulting specific heats are that, except for $\Delta \leq T_0$, the main peak is shifted to lower in temperature, and its height is decreased from the isolated Schottky peak. The most prominent feature is the height decrease, and for several compounds (CeAl$_3$, CeAl$_2$, CeCu$_4$) there is qualitative agreement in this aspect. The shift in peak position becomes less pronounced as $\Delta$ becomes smaller, and, in fact, becomes positive for $\Delta \leq 0.5T_0$ due to the overlap of the Kondo peak. However, even using the shape of the specific-heat curve to estimate $\Delta/T_0$ there is not good agreement.

The experimental peak is at a higher temperature for CeAl$_3$ ($\Delta/T_0 \approx 1.5$), CeAl$_2$ ($\Delta/T_0 \approx 1.2$), and CeCu$_4$ ($\Delta/T_0 \approx 2$). The position of the peak is correct for CeRu$_2$Si$_2$, but the peak height is much too high. CeCu$_4$ seems the only material with qualitative agreement in position and a peak height at least not higher than the Schottky.

Desgranges and Rasul have applied their model to (LaCe)$_{3-x}$, assuming a crystal-field splitting of $\Delta/T_0 = 0.7$. They get good agreement with the experimental data at low temperatures ($T < 0.2$ K), but the peak is somewhat large in magnitude and above 0.5K the calculated curve drops off too sharply. Although better than that of no crystal-field splitting, the fit is not great, and, in particular, would seem to give too low a value for the limiting high-temperature entropy. Desgranges and Rasul also fit their three-doublet calculations to the case of CeAl$_3$. However, the experimental data they cite shows spurious magnetic phase transitions due to impurities in the sample. These extraneous peaks occur right at the temperature regime separating Kondo- from Schottky-dominated behavior, making comparison to theory difficult.

In summary, a shoulder-plus-peak structure is indeed seen in Ce compounds, and in this respect there is qualitative agreement with the theory of Desgranges et al. However, the decrease in peak height from a straight Schottky behavior is only seen in a few compounds, and for these the peak position is at too high a temperature. This may be accounted for by uncertainty in the crystal-field splitting. Using the shape of the specific heat to find $\Delta/T_0$ gives qualitatively correct values of $T_0$. As it stands, the calculations are only applicable to Ce compounds.

Fermi-liquid solid regime ($T \ll T^*_f, T_0$). At very low temperatures, interactions between the $f$ atoms become noticeable. The clearest evidence for this is the crossover in the electrical resistivity with decreasing temperature from a rising (Kondo-like) resistivity to a dropping resistivity as in ordinary metals. (We expect the resistivity to show interaction effects at a higher temperature than equilibrium properties due to the fact that the resistivity of Bloch states must be zero at zero temperature. This argument hinges on the fact that the resistivity is very sensitive to impurities while the specific heat, susceptibility, and other transport properties are not. Accordingly, a small amount of impurity will destroy the Bloch-coherence at low temperatures and, we expect, strongly effect the resistivity at higher temperatures. In fact, the resistivity typically turns over at $T_0$.) The principal difference from ordinary metals is that the $T^2$ coefficient $\alpha$ in $\rho(T) = \rho(0) + \alpha T^2$ is many orders of magnitude larger than in metals such as Pd. Roughly, it appears that $\alpha \propto (1/T^2)^2$.

This $T^2$ dependence suggests a Fermi-liquid description. But if something that simple were true, then it is hard to understand the additional temperature-dependent structure that is seen in various properties for $T/T^*_f < 10^{-2}$. Figure 1 shows a compilation of equilibrium- and transport data for CeAl$_3$. A simple Fermi-liquid picture would require that the specific heat, the electronic thermal conductivity, and the thermopower be linear in temperature while the resistivity would go as $T^2$. According to Fig. 1, this state of affairs occurs for temperatures below 0.07 K, i.e., for $T/T^*_f < 0.003$. A Fermi-liquid theory of such limited range is not very useful.

What one would want is a theory capable of reproducing the lowest temperature bump in $C(T)/T$ (Ref. 15) and showing the downturn in the thermopower, not to mention the temperature-dependent structure in the Hall effect. A possible model would involve a renormalized band structure of width $T^*_f$ in which a phenomenological interaction between $f$ electrons is added to a conventional band-structure calculation for the remaining electrons. There are preliminary calculations for such a model; they show Van Hove-like singularities in the narrow quasi-particle $f$ band crossing the Fermi level. Whether the renormalized band structure, together with model scattering rates, could explain the low-temperature data is still to be tested.
Finally we should point out (1) the considerable sensitivity of the low-temperature properties to pressure [i.e., a peak in $C(T)/T$ for CeAl$_3$ (Ref. 19)] and magnetic field [e.g., a peak in $C(T)/T$ for CeCu$_6$ (Ref. 20) and for CeAl$_3$ (Ref. 21), (2) the sensitivity of the Hall effect (to impurities) in several heavy-electron metals (UPt$_3$, UAl$_2$, CeAl$_3$, and CeRu$_2$Si$_2$),$^{16}$ and (3) the extraordinary influence of impurities [e.g., Th in UBe$_{13}$ (Ref. 22) produces a second transition, whereas Cu in U$_2$Zn$_{17}$ (Ref. 23) and Ni in UCu$_3$ (Ref. 24) remove the magnetic transition].

While we have called these three regimes the "standard model" of heavy electrons (cf. Table IV), we would stress that no theory connects them. In this paper we confine ourselves largely to the high-temperature regime. We present new data for U$_2$Zn$_{17}$ and CeCu$_6$ and examine them for evidence of crystal fields and independent spins, i.e., are the data consistent with the standard model at high temperature?

III. EXPERIMENTAL METHODS

Specific heat measurements were performed using the standard heat-pulse method in a $^4$He cryostat.$^{25}$ The samples were produced at the Los Alamos National Laboratory. The masses of the three samples of U$_2$Zn$_{17}$ were 0.7750, 0.2933, and 0.2555 g, respectively, those of the Th$_2$Zn$_{17}$ samples were 1.6998 and 0.5300 g, and the CeCu$_6$ and LaCu$_6$ were 0.5805 g and 1.486 g, respectively. The third U$_2$Zn$_{17}$ sample had been measured previously.$^{26}$ The thermal sample-to-bath time constants ranged from 60 s at 2.5 K for the smaller Th$_2$Zn$_{17}$ sample, to 2000 s at 80 K for the larger samples. The internal time constants were much less than 1 s at 2.5 K and about 10 s at 80 K for the larger samples. Below 10 K, the heat capacity of the addenda was much less than 1% of the total heat capacity, but by 70 K the addenda accounted for almost 10% of the total heat capacity for the smallest samples. This, however, is not a problem because the addenda heat capacity is known to better than 5%.$^{25}$ The temperature of the sample was measured with a chip (about 0.5 mg) of a 1200-Ω Allen-Bradley resistor, calibrated on every cooldown against a germanium-resistance thermometer below 40 K, and against a platinum-resistance thermometer above 20 K. The germanium- and platinum-resistance thermometers agree to within 0.1% in the range of overlap; both were calibrated against a Rh:Fe-resistance thermometer with a calibration traceable to the National Physical Laboratory in England.

The dominant source of error in the measurement is the internal time constant, which also includes a sample-holder-to-sample time constant. At the highest temperatures of measurement (80 K), during the first few internal time constants (a few tens of seconds, as stated above) the sample holder is somewhat hotter than the sample. This causes the heat flow into the sample to be overestimated, as some heat is lost to radiation and conduction through the weak link before it reaches the sample. We calculate that this error will cause about a 1% overestimation of the measured heat capacity of the sample. This error, though, should scale with the heat capacity of the sample, and to a large extent will cancel in the subtraction of the specific heat of the non-heavy-electron counterpart. The accuracy of our measurements has been checked by measuring a sample of pure copper, and can also be seen in the reproducibility of the specific heat of the samples of U$_2$Zn$_{17}$ of different masses, and of Th$_2$Zn$_{17}$ of different masses.

At higher temperature the heat capacity of the phonons exceeds that of the electrons, and the subtraction of the lattice becomes more susceptible to error. For U$_2$Zn$_{17}$, at about 17 K the electronic specific heat is half the total, at 36 K it is one-sixth, and at 50 K it is one-tenth. Thus, after subtracting the lattice contribution, assuming a random 1% error, there is about a 10% uncertainty in the electronic specific heat at 50 K, and about a 20% uncertainty at 70 K. The uncertainty is similar for CeCu$_6$.

A separate determination of the phonon density of states would certainly be a useful check on the lattice-subtraction procedure used here. Unfortunately, there is
very little neutron-scattering data at all, and what there is has limited usefulness. In the case of UB\(\text{Be}_{13}\) there have been two measurements. One triple-axis-spectrometer measurement\(^{23}\) of the lower-lying acoustic modes at room temperature and at 10 K concludes that they are consistent with scaling from pure beryllium (by replacing the Be mass with the mass of Be\(\text{U}_{1/13}\)). Time-of-flight measurements\(^{26,29}\) at 300 K and 8 K were also able to determine an optic mode at 13 meV. The lattice-vibration spectra of ThB\(\text{Be}_{13}\) and UB\(\text{Be}_{13}\) are very similar, suggesting that using ThB\(\text{Be}_{13}\) as a guide to all the phonons in UB\(\text{Be}_{13}\) is reasonable. Finally, a time-of-flight measurement\(^{26}\) is available for UP\(\text{t}_{3}\) at 300 K and preliminary measurements at 8 K suggest no dramatic changes in the acoustic and optic modes.

IV. DESCRIPTION OF RESULTS

Shown in Fig. 2 are the measured specific heats for U\(\text{Zn}_{17}\), Th\(\text{Zn}_{17}\), Ce\(\text{Cu}_{6}\), and La\(\text{Cu}_{6}\), plotted log-log versus temperature. The dominance of the electronic specific heat at the lower temperatures and of the phonon specific heat at high temperatures is clear; the non-heavy-electron counterpart specific heat is orders of magnitude smaller than the heavy-electron specific heat at the lowest temperatures, but only about 10% smaller at 70 K. We have plotted in Fig. 3 the difference, \(\Delta C(T)\), between the total specific heat and the phonon specific heat (as estimated using the specific heat of the non-heavy-electron counterparts), divided by the temperature \(T\). The specific heats of U\(\text{Zn}_{17}\) and Th\(\text{Zn}_{17}\) have been measured before\(^{26,26}\) up to 17 K. The specific heat of Ce\(\text{Cu}_{6}\) has been measured twice before, by Steward, Fisk and Wire\(^{21}\) and by Fujita, Satoh, Onuki, and Komatsu\(^{20}\). Several observations can be made immediately.

For U\(\text{Zn}_{17}\), the anti-ferromagnetic transition at 9.7 K is very sharp. The specific heat at the transition follows a typical \(\lambda\) curve with a smooth high-temperature tail. There does appear to be an entropy balance at the transition; that is, the total entropy through the transition, i.e., the area under the \(C(T)/T\) curve, does appear to be the same as the area under the curve generated by extrapolating \(C(T)/T\) to \(T=0\) from above the transition. The anomalously high electronic specific heat extends to the highest temperature of measurement, 70 K. Below the transition at 9.7 K, our measurement of the specific heat of U\(\text{Zn}_{17}\) and that reported earlier\(^{26}\) are indistinguishable. However, the electronic specific heat above 9.7 K is quite different, both in the shape of the transition, and in magnitude, by a factor of about 50%. The previous researchers also found that the transition had absolutely no high-temperature tail, and entropy balance was not satisfied. Because of this discrepancy, another sample (sample B) was produced at Los Alamos, and measured at Cornell, and its specific heat was found to agree with that of our first sample (A). In order to determine whether the disagreement between our measurements and those reported earlier was due to a strange sample dependence or to experimental error, we asked H. R. Ott for his sample, which he kindly supplied. Our measurements on his sample agreed with our other samples, and we conclude there are no unusual sample dependences between samples prepared more than 1 yr apart. The sample has been sent back to Zurich, where it will be remeasured as a final check.

Below about 20 K, there are no detectable sample dependences at all. Between 20K and 50 K, though, there is a small difference in the electronic specific heat of the samples which we cannot attribute to measurement uncertainties. Above 50 K the data start to show the scatter that is associated with the uncertain subtraction of the phonon specific heat. Differences above 50 K thus cannot be attributed to sample dependences, but may simply be due to small random errors in the data.

The Ce\(\text{Cu}_{6}\) specific heat clearly displays the large \(\gamma\) characteristic of heavy-electron materials. The Ce\(\text{Cu}_{6}\) electronic specific heat shows no sharp transitions as it is neither superconducting nor magnetic. There is, however, a broad bump in \(C_{\text{el}}/T\) centered near 26 K, and another near 60 K. The latter, though, is not experimentally significant, as it is smaller than the experimental uncertainty due to the lattice subtraction. The broad bump at 20 K will be discussed later and is attributed to the CEF levels. The measurement of Ce\(\text{Cu}_{6}\) by Fujita,
et al.\textsuperscript{20} extended to 70 K, high enough to deduce the electronic entropy, but above about 50 K the specific heat showed an anomalous upturn, as it would if radiation difficulties in the measurement were present. Our measurements do not show this upturn at high temperature, but do agree with the previous measurements below 40 K.\textsuperscript{32} Our electronic specific heat agrees reasonably well with that reported by Fujita et al., even in the temperature range of their anomalous upturn. This supports our explanation that their upturn was systematic and thus, to a large extent, cancelled upon lattice subtraction.

The subtraction of the lattice heat capacity using the non-heavy-electron counterpart leads to uncertainty in the electronic specific heat, not only for the above experimental reasons, but for more fundamental reasons as well. It is not true that the density, elastic constants, and lattice constants are identical for the counterpart material. See Table V for the densities, crystal structures, and lattice constants of several heavy-electron materials and their nonheavy counterparts. For the case of U\textsubscript{2}Zn\textsubscript{17} the crystal structure is the Th\textsubscript{2}Zn\textsubscript{17} structure, but the lattice constants are between 0.5\% and 1.5\% smaller for the Th\textsubscript{2}Zn\textsubscript{17}. The density of U\textsubscript{2}Zn\textsubscript{17} is about 2\% higher than that of Th\textsubscript{2}Zn\textsubscript{17}. We do not know the difference in the elastic constants. The Debye formalism for the lattice specific heat predicts that the low-temperature molar specific heat has the following dependence:

$$C_v \sim V \left( \frac{\rho}{E} \right)^{3/2}.$$  

Here, $\rho$ is the density, $V$ is the volume of a unit cell, and $E$ represents an average elastic constant. Thus, assuming the elastic constants for the two compounds are the same (not true, but we do not know the elastic constants), we estimate from the lattice and density differences that the U\textsubscript{2}Zn\textsubscript{17} should have about a 1\% higher Debye lattice specific heat than the Th\textsubscript{2}Zn\textsubscript{17}. For the case of CeCu\textsubscript{6}, the crystal structure is the same as LaCu\textsubscript{6}, and the lattice constants of CeCu\textsubscript{6} are about 0.7\%–0.9 \% smaller than those of LaCu\textsubscript{6}. The density of CeCu\textsubscript{6} is about 2.5\% higher than the density of LaCu\textsubscript{6}. Thus, by using the specific heat of LaCu\textsubscript{6}, we have slightly underestimated the Debye lattice specific heat of CeCu\textsubscript{6} by about 1.4\%, based only on the differences in the density and the lattice constants. Again, for CeCu\textsubscript{6} and LaCu\textsubscript{6} we do not have elastic constants so we cannot estimate their effects.

An even more fundamental objection to the subtraction is that the heavy-electron character could have a non-negligible effect on the phonons directly, so that the lattice specific heat would be substantially different from

<table>
<thead>
<tr>
<th>Compound</th>
<th>Crystal structure</th>
<th>Density (g/cm(^3))</th>
<th>Lattice parameters</th>
<th>Volume (Å(^3))</th>
<th>Units (per cell)</th>
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<tr>
<td>CeAl\textsubscript{3}</td>
<td>Ni\textsubscript{3}Sn (hex)</td>
<td>2.521</td>
<td>8.54</td>
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<td>ThCr\textsubscript{2}Si\textsubscript{1} (tet)</td>
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<td>LaCu\textsubscript{6}Si\textsubscript{2}</td>
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<td>CeCu\textsubscript{6} (orth)</td>
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<tr>
<td>U\textsubscript{2}Zn\textsubscript{17} &amp; Th\textsubscript{2}Zn\textsubscript{17} (rhom)</td>
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<td>8.983</td>
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<tr>
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<td>10.60</td>
<td>7.036</td>
<td>348.3</td>
<td>4</td>
<td></td>
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</tbody>
</table>

\*Reference 65.
\*Reference 66.
\*Reference 67.
\*Reference 68.
\*Reference 69.
\*Reference 70.
\*Reference 71.
\*Crystal parameters, volume of cell, and formula units per unit cell are reported for the hexagonal structure formed of two rhombohedral unit cells.
\*Reference 72.
\*Reference 73.
the Debye prediction. This we cannot estimate without a direct measurement of the density of states of the phonons. However, at temperatures around 10 K, the phonon contribution from the non-heavy-electron material is almost an order of magnitude smaller than the total specific heat of the heavy-fermion compound. Even if substantially altered, the heavy-electron-phonon part will probably still be quite small compared to the electronic contributions, and will not affect the specific heat. At higher temperatures the phonon contribution becomes substantial, as does the (subtraction-based) error, and the assumption here is that the purely electronic specific heat will still be within the range of uncertainty.

Plotted in Fig. 4 are the normalized integrated entropy and associated number of degrees of freedom (\(N_{\text{dof}}\)) for \(\text{U}_2\text{Zn}_{17}\) and \(\text{CeCu}_6\). The entropy is simply the area under the curves in Fig. 3, and the number of degrees of freedom is then \(\exp(S/R)\), where \(R\) is the molar gas constant. Error in the lattice specific heat subtracted will clearly have an effect on the integrated entropy of the electrons. For \(\text{U}_2\text{Zn}_{17}\), roughly, a 1% underestimation of the lattice specific heat to be subtracted will cause the calculated number of degrees of freedom to be overestimated by 1 at 70 K. Thus, if the lattice specific heat of \(\text{U}_2\text{Zn}_{17}\) is larger than \(\text{Th}_2\text{Zn}_{17}\) by 1%, as we have estimated above from the density and lattice constants, we should report the number of degrees of freedom at 70 K to be 11 and not 12. For \(\text{CeCu}_6\), roughly, a 1% underestimation of the lattice specific heat will cause the calculated number of degrees of freedom to be overestimated by about \(\frac{1}{4}\) of a degree of freedom at 80 K. Therefore, if the \(\text{CeCu}_6\) does have a 1.4% larger lattice specific heat than \(\text{LaCu}_6\), as we have estimated from the differences in the densities and lattice constants, then we should report the number of degrees of freedom as 3.9 and not 4.3 at 80 K. This analysis is meant only as a guide to the size of the uncertainty. Without the precise phonon density of states, or at least the elastic constants, a more precise analysis cannot be done.

\[ V. \ \text{DISCUSSION} \]

We want to focus on two aspects of the high-temperature (\(T > T_0\)) part of the standard model: (1) how many degrees of freedom are seen and (2) what the evidence for CEF levels is. The first provides a crude test of the standard model and the second a more sophisticated one. In the case of both Ce and U compounds we assume we are in the LS-coupling regime; this is probably a reasonably good approximation since the spin-orbit splitting is 0.2 eV for Ce and \(-0.8\) eV for U. (The relevant comparison is the ratio of the spin-orbit coupling to the \(F^2\) integral deduced from the spectra or Hartree-Fock calculations. These ratios are 0.001 and 0.086 for Ce and U, respectively.) Nonetheless, since it will turn out that we see too many degrees of freedom for U, there is a possibility that these materials are in an intermediate-coupling regime in which the number of degrees of freedom might be larger than \(2J + 1\).

\[ A. \ \text{Entropy} \ \Delta S(T) \]

Figure 4 shows the entropy of \(\text{U}_2\text{Zn}_{17}\) relative to \(\text{Th}_2\text{Zn}_{17}\) and of \(\text{CeCu}_6\) relative to \(\text{LaCu}_6\). Under the assumption that the only contribution to this difference is due to the \(f\) electrons, then we would expect to recover the full number of degrees of freedom associated with the \(f\) electrons at a temperature large compared to \(T_0\) and \(\Delta\).

\(\text{CeCu}_6\): The evidence for the standard model is fairly clear for \(\text{CeCu}_6\). \(\Delta S/R \) exceeds \(\ln 4\) near 80 K, which is larger than \(T_0 - 25 \) K and, as discussed next, smaller than the estimated CEF splittings. The peak in \(\Delta C(T)\) occurs at 26, suggesting a CEF level at 60 K. For an \(f^1\) configuration, \(J = \frac{5}{2}\), i.e., the number of degrees of freedom is 6. Thus, \(\Delta S \geq \ln 4\) is consistent with the standard model; a result which is also the case for the data of \(\text{CeAl}_3\) and \(\text{CeCu}_3\text{Si}_2\) (cf. Table IV).

\(\text{U}_2\text{Zn}_{17}\): The situation is much less clear for \(\text{U}_2\text{Zn}_{17}\). At 70 K, \(\Delta S/R \) exceeds \(\ln 10\) per U atom. This very large number poses two problems for the standard model:

(1) The first problem is that a value of \(\ln 10\) is already the largest number of degrees of freedom we can readily imagine for independent U atoms. The two most likely configurations for U are \(f^0\) with a ground state \(J = 4\) and \(f^1\) with \(J = \frac{5}{2}\). These two ground-state terms have 9 and 10 degrees of freedom, respectively. Nonetheless, \(\Delta S/R > \ln 10\) at 70 K. This fact has caused us to reexamine how the lattice and non-\(f\)-electron contributions should be subtracted. Still, as indicated in Section IV, there seems to be no obvious way to substantially reduce \(\Delta C(T)\) or \(\Delta S(T)\).

(2) The second problem in understanding the large value of \(\Delta S(T)\) is that it occurs at too low a temperature compared to \(T_0\) and \(\Delta\). Both of these energy scales are difficult to estimate. \(x^{-1}\) is only roughly linear in \(T\) between \(0.6T_0\) and \(3T_0\). Accordingly \(T_0 = 65\) K has an uncertainty, but it is unlikely to be smaller by an order of magnitude. Any observable CEF levels must be larger than 350 K according to neutron-scattering exper-
B. Specific heat $\Delta C(T)$

The specific heat provides a more detailed test of the standard model than $\Delta S(T)$ provided. As a point of departure we note that the previous attempts to fit the electronic specific heats of CeAl$_3$ (Ref. 35), CeCu$_2$Si$_2$ (Ref. 36), CeCu$_6$ (Ref. 20) [for $\Delta S(T)$ only], and UBe$_1$_3 (Ref. 3) are based on the addition of two peaked structures, one due to the Kondo specific heat of the low-lying doublet and the second due to the Schottky contribution of the next CEF doublet. This approach is a little simplistic since the two contributions do not add so simply. But, in the absence of a detailed theory it is a reasonable starting point.

**Fitting procedures.** We have used both a CEF-level scheme and, in the case of U$_2$Zn$_{17}$, a density-of-states scheme to fit the measured specific heat. In the crystal-field scheme we use the following pattern of levels: for $f^1$ in CeCu$_6$ we have three doublets whose two spacings can be varied to achieve a fit. In U$_2$Zn$_{17}$ there is a choice of two configurations, both of which we have tried: for $f^2$ there are three doublets and three singlets, while for $f^3$ there are five doublets. Then one just uses a generalization of the Schottky specific-heat formula (see Introduction) and adjusts the splittings for the best fit. While the whole process could be computerized, the process goes quite quickly on a trial and error basis.

U$_2$Zn$_{17}$: Here we also tried fitting the specific heat with a distribution of levels described by a density of states. In particular, we approximate the density of states of the many-body conduction band with a sum of several Lorentzians. The band has a total weight of nine or ten states per U atom (for $f^2$ or $f^3$, respectively), but the (temperature-dependent) chemical potential is set to give a constant filling of 1. That is, in analogy with the crystal-field levels, each of which corresponds to a two- or three-electron state, the many-body band in its ground state has a unique energy level associated with a many-body (two- or three-electron) state. But in contrast, while the CEF scheme has Boltzmann statistics, the band scheme has Fermi statistics.

We will show that the entropy of this strongly correlated density-of-states model is very similar to what we get for the CEF model, but with a small addition ($\leq 1$) which increases the entropy sufficiently to account for the experimentally large entropy contributions. For simplicity we consider the case of $f^3$ where the total degeneracy $N$ is 10. The entropy per U atom has the form

$$\frac{\Delta S}{R} = -N \sum_\epsilon \left[ f_\epsilon \ln(f_\epsilon) + (1 - f_\epsilon) \ln(1 - f_\epsilon) \right].$$

where $f_\epsilon = (\exp[-(\epsilon - \mu(T))/k_B T] + 1)^{-1}$. The chemical potential $\mu(T)$ is adjusted to maintain the fractional occupancy of the band, which in the case of $f^3$ is $1/N = 1/10$ (and would be $1/2$ for $f^5$). At temperatures large compared to the bandwidth, $(\exp[-(\epsilon - \mu(T))/k_B T] + 1)^{-1}$ is 0.1. From this we can deduce that the entropy at high temperatures reduces to $10 + 9 \ln(\frac{10}{3})$ [i.e., $\sim \ln(26)$], which is somewhat larger (by 0.9) than the CEF model, which gives $10N$ for the $f^3$ case. In general, for large $N$ the degeneracy for the Fermi statistics model is a factor of $e$ more than that of CEF (Boltzmann).

We should stress that this is a very unusual band model, one in which there are very strong correlations. In fact, there is no actual model which contains the features of “quasi-itinerant” $f^3$ states. On the contrary, the phrase “band model” usually implies a set of largely independent electrons. Such a model leads to large entropies. For example, two independent electrons in a band with six states (as if a crystal-field splitting had moved the rest of band to very high energy) would have a high-temperature entropy of $2 \ln 3 + 4 \ln \left(\frac{1}{2}\right) - \ln(46) = 3.8$, whereas if the band held ten electrons the entropy would be $\sim \ln(149)$, which is almost twice the largest entropy seen so far (5.0). It is numbers such as these that makes it difficult to accept any over-simple renormalized band model. As the temperature increases, the band must broaden rapidly to prevent the entropy from reaching its “ionized” atom limit at room temperature.

CeCu$_6$: From the CeCu$_6$ specific-heat data we can only deduce the possible presence of one high-lying doublet. (The data cannot be used to extract a second crystal-field level.) Figure 5 [$\Delta C(T)$ versus $\ln T$] shows a reasonable fit to the overall pattern of the data, but the theory is higher and narrower than the data. We could improve the fit by broadening the high-lying CEF levels, but defer using that approach until analyzing the U$_2$Zn$_{17}$ data.

![Figure 5](https://example.com/fig5.png)

**FIG. 5.** Fit of the CEF model (solid line) to $\Delta C(T)$ data (triangles) for CeCu$_6$ relative to LaCu$_6$. The experimental uncertainty at higher temperatures ($> 30$ K) is about the same size as the scatter in the points. The inset shows the level scheme of three doublets separated by 42 and 79 K.
U$_{2}$Zn$_{17}$: In Fig. 6 we see the fit for a CEF pattern for U$_{2}$Zn$_{17}$. Note that in order to give any agreement whatsoever we must scale the calculated curve (solid line) by a factor of 1.5 (dotted line). This illustrates the point made in the preceding section: there are more degrees of freedom in the data than are consistent with a CEF model.

In contrast, Fig. 7 shows the good fit that results from using the band density of states shown in the inset of the figure. Two Lorentzian peaks were found necessary to fit the data. Similarly, Fig. 8 shows the fit for CeCu$_{6}$ obtained by using a two-peak structure in the density of states (inset). (Note that the experimental uncertainty for temperatures greater than about 30 K is roughly the size of the scatter of the points.) For both materials, a second peak is necessary to account for the low-temperature shoulder seen in the data. These densities of states should be viewed as only illustrative since any such renormalized band would vary strongly as the temperature increases through $T_{0}$. We include them merely to stress the difficulties faced by any theory attempting to explain the full temperature dependence of any property.

VI. CONCLUSIONS

The specific heats and entropies of the heavy-electron metals at high temperatures ($T \geq T_{0}$) suggest the following.

1) In Ce-based materials a crystal-electric-field-split $f^{l}$ state is consistent with the data. However, the lack of any solid observation of a CEF level in the needed range, less than 100 K, (with the exceptions of CeAl$_{2}$ and CeAl$_{3}$), suggests that if there are CEF levels present, the effect of the Kondo coupling is so strong as to make them unobservable by neutron scattering. The low-temperature shoulder in the data further indicates a broadening of the levels.

2) In U-based materials no CEF levels have been directly observed, although in two materials (UBe$_{13}$ and U$_{2}$Zn$_{17}$) the specific heat is roughly consistent with their existence. However, especially in the case of U$_{2}$Zn$_{17}$, the entropy is too large for traditional CEF even up to degeneracy 10. A model band density of states with a splitting of $\sim$ 100 K gives a good fit to the data and suggests that the additional entropy may be a sign of
greater correlations in these materials, with perhaps an effective hopping between sites giving greater degeneracy and accounting for the different statistics. Clearly, a more ambitious study of crystal-electric-field levels is warranted, especially for U compounds.

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4In the strongly mixed-valent regime, charge fluctuations would strongly affect the phonons; hence we would not expect the subtraction procedure to be accurate in this regime. Heavy-electron metals are believed to correspond to nearly integral valence in which case the charge fluctuations should modify the phonon spectrum only slightly from those of the comparison compound.


6W. Felsch, Z. Phys. B 29, 211 (1978) (we have extracted the values of $T_0$ cited in the text for Ce$_x$La$_{1-x}$B$_6$).


10A. P. Murani, K. Knorr, and K. H. J. Buschow, *Crystal Field Effects in Metals and Alloys*, edited by A. Furrer (Plenum, New York, 1977), p. 268 (CeAl$_5$); to extract the splitting requires a difficult background subtraction. A polarized-neutron measurement would be a useful check on this work.

11D. L. Cox has suggested (private communication) that in U materials the lowest CEF level may be a nonmagnetic electric-quadrupole doublet. If that should prove correct, a more complicated Kondo-type analysis must be performed.


13H.-U. Desgranges and J. W. Rasul (private communication).


15The bump in $\kappa$ is roughly consistent with the thermal resistivity being the sum of contributions from impurity scattering and electron-electron scattering.


23J. O. Willis (private communication).


32Fujita et al. (Ref. 20) also noted this anomaly and are in the process of reexamining their samples.

33J. O. Willis (private communication) has informed us that preliminary analysis of dilute U($\sim$5%) in Th$_2$Zn$_{17}$ yields a similar $T_0$ as $\text{U}_2\text{Zn}_{17}$ itself.

34G. Aeppli (private communication) has observed no inelastic-neutron-scattering features which would be associated with undamped crystal-electric-field levels in U$_2$Zn$_{17}$ below $\sim$ 350 K. However, since $T_0$ is comparable to the position of the peak in $\Delta C/T$, it might be that Kondo effects could obscure the effects of CEF levels.


37 We are indebted to Dr. J. Sierro, Dr. D. Jaccard, and Dr. A. Amato, who made this compilation of data for us.


39 D. Jaccard (private communication) measured the resistivity from a sample cut from the same ingot that supplied samples for the thermal-conductivity and thermopower measurements (CeAl$_2$).


42 We are indebted to M. B. Maple for estimating these values of $T_F^*$ and $m^*/m$. $T_F^*$


48 J. O. Willis (private communication) (U$_2$Zn$_3$). Some additional evidence that the CEF levels are greater than room temperature is provided by the inverse parallel and perpendicular (with respect to the c axis) susceptibilities having the same slope versus $T$ to 300 K (with intercepts of $-130$ and $-95$ K, respectively). This suggests that whatever CEF level is responsible for the anisotropy must be greater than 300 K, because at temperature greater than that splitting the susceptibilities should converge.


