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Authors

Fisk, Z
Thompson, JD
Ott, HR

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INVITED PAPER

HEAVY-ELECTRONS: NEW MATERIALS

Z. FISK, J.D. THOMPSON

Los Alamos National Laboratory, Los Alamos, NM 87545, USA

and H.R. OTT

ETH-Honggerberg, 8093 Zürich, Switzerland

The large γ of heavy-electron materials is predominantly a single-ion effect: $\gamma \propto 1/T_K$. The most interesting physical effects occur in the low-temperature coherent state of a chemically ordered lattice of these ions. The large- γ state can be strongly quenched by magnetic order, and we argue that this effect is more pronounced for Ce than U materials. We discuss recent work in this light, and address the interesting possibility of heavy-electron materials in which charge fluctuation effects may be important.

1. General considerations

The clear-cut examples of heavy-electron behavior are found in compounds containing f-elements. Among these, Ce, Yb and U are very much the most common elements forming such materials. It is these same elements which are known to be capable of exhibiting the Kondo effect in dilute alloys, and, indeed, the high temperature properties of heavy-electron systems appear to be those of a collection of independent Kondo impurities.

A convenient qualitative framework within which to discuss the properties of heavy-electron systems is provided by Kondo ideas. The high temperature local-moment behavior in heavy-electron systems develops smoothly on cooling into the heavy-electron behavior. Looked at from the other direction, the spin-degeneracy entropy of the high-temperature local moments grows continuously from the very large γT conduction electron specific heat. This happens over a temperature range of order T_K , the Kondo temperature. A rough estimate gives $\gamma \approx (k \ln D)/T_K$ per f-atom, where D is the f-moment degeneracy. The lower T_K is, the higher the γ .

Roughly speaking, large γ is a single-ion property, being generated by the f-moment fluctuations. What competes with the development of large γ is magnetic order, mediated by the RKKY interaction. When T_K is very low, we might expect magnetic ordering to occur above T_K . And when this happens, the internal magnetic field felt and

the f-sites due to the establishment of the long-range magnetic order will partially quench the Kondo effect there, reducing the large γ of the material.

This simplified reasoning suggests a difference between Ce and U materials. We expect the comparison of RKKY and Kondo energy scales to vary as $T_{RKKY}/T_K \approx (\rho J)^2 / \exp(-1/\rho |J|)$.

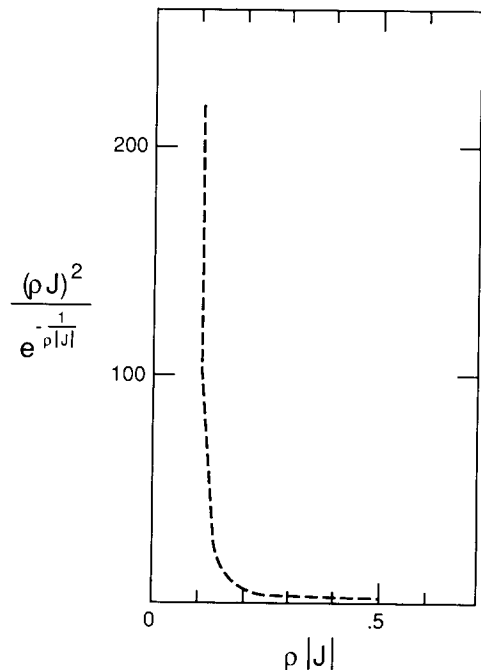


Fig. 1. Plot of T_{RKKY}/T_F versus $\rho |J|$.

where ρ is the electronic density of states and J and f-electron-conduction electron mixing matrix element. We plot this ratio as a function of $\rho|J|$ in fig. 1. Typical values of T_K are 1 and 10 K for Ce and U systems, respectively. Using $T_K = T_F \exp(-1/\rho|J|)$ with a Fermi temperature of 10^4 K, the corresponding $\rho|J|$ are 0.11 and 0.14. This leads to the crude estimate that T_{RKKY}/T_K is ≈ 5 times larger for Ce than similar U material. What this means is that the establishment of magnetic order in the heavy-electron Ce materials will be much more effective in reducing γ than in U materials. This seems to be true: $\gamma \rightarrow \gamma/3$ when typical heavy-electron U-antiferromagnets order, while the γ 's extrapolated from above T_N for Ce antiferromagnets are very much reduced below T_N . However, it is difficult to determine γ above T_N because we have no clean criterion for distinguishing an upturn characteristic of large γ from an upturn in C/T associated with the phase transition.

2. Chemical and crystal structure effects

It is clear that the chemical environment can have a strong influence on γ . One tends to think of this as a local effect: atoms in the first coordination polyhedron of the f-ion dominate its behavior. In fig. 2 we show where binary U heavy-electron compounds are found in the periodic table. We see that elements near and to right of the border between d- and sp-elements form such compounds with U. One way to think about this is as a progressive localization of the f's on moving out of the d- and into the sp-elements, due to

decreasing f-hybridization with the conduction electrons in the compounds.

Compilations of heavy-electron materials suggest that certain crystal structures are better suited to the forming of a heavy-electron ground state than others. It is possible, of course, that this statistic results from the non-random way in which experimentalists go about looking for new materials. But there is also a kind of rationale for this which can be advanced. Namely, T_{RKKY} involves in addition to the $(\rho J)^2$ factor discussed above, another multiplicative factor which is the sum of all the RKKY pair interactions with a given f-site. This sum depends on both the geometry of the crystal lattice and the Fermi momentum. It may happen that this sum may tend to be particularly small for a particular crystal structure, and this could help T_K to dominate T_{RKKY} . A related remark is that some lattices are inherently magnetically frustrated: the fcc-lattice and the plane triangular lattice, for example. Again, such a situation could favor the development of large γ .

Arguments of this kind have been given by Coles et al. [1] for the DO_{19} structure. The heavy-electron materials CeAl_3 and UPt_3 adopt this structure, which is the hexagonal stacking of Cu_3Au . It is argued that the frustrated nature of possible magnetic order in this structure is indicated by the small ratio of $T_N/\theta_p \approx 1/5$ for isostructural GdAl_3 . This may also be related to the recently discovered anomalous magnetic behavior of CeAl_3 below 2 K [2]. The Cu_3Au structure itself does not appear especially favorable for the formation of a heavy-electron ground state, and it is interesting that the mixed hexagonal-cubic variant DO_{24} adopted by UPd_3 leads, in this case, to a well localized f-moment, not a heavy electron material.

3. Materials

3.1. C15 and related structures

The C15 cubic Laves phase structure is found for many intermetallics at the AB_2 stoichiometry: CeAl_2 and UAl_2 are examples. The A-atoms occupy a diamond lattice: two fcc-lattices shifted from each other by $1/4$ of the cube body-diagonal. This puts each A-atom at the center of a tetrahedron of other A-atoms. While both CeAl_2

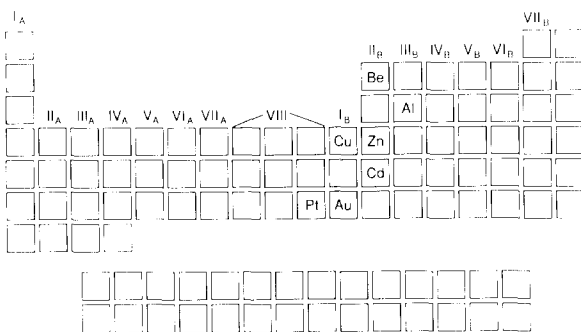


Fig. 2. Occurrence of heavy-electron binary compounds in the periodic table.

and UAl_2 are at the lower edge of heavy-electron γ 's, it is often noticed that the heavy-electron ground state is less likely when the f-atom has like-atom neighbors. We expect, incidentally, this to be a more stringent condition for U- than Ce-compounds.

A variant of the structure, the C15_b or AuBe_5 -structure, has one of the two fcc-lattices occupied entirely by non-A atoms, either the B-atom or a third-atom. This gives the stoichiometry $\text{A}_{0.5}\text{B}_{0.5}\text{B}_2$ (AB_5) or $\text{A}_{0.5}\text{C}_{0.5}\text{B}_2$ (ACB_4). In these cases, the A-atom no longer has A near neighbors: it is possible to tune the behavior of A to some extent with appropriate choice of atom for the other fcc-site, provided, of course, that the compound will form.

The clearest successes in looking for heavy-electron behavior in this C15_b structure have come from starting with compounds forming at AB_5 stoichiometry and substituting for one B-atom, an atom whose radius is intermediate between the radii of A and B. An example is given by UAuPt_4 whose $\gamma = 720 \text{ mJ/mol U K}^2$. The parent compound is UPt_5 for which the $\gamma = 90 \text{ mJ/mol U K}^2$ (fig. 3) [3]. There is no hard proof as yet that Au occupies the special fcc-lattice position in this compound, but the electrical resistance ratio suggests that the compound is atomically ordered. It is worth pointing out that atomically ordered heavy-electron systems are in many ways of more interest than the disordered ones, in that the ordered ones can be expected to evidence more of the unusual low temperature properties which depend on the establishment of coherence.

A second example comes from the Yb-Cu system. All of the compounds in this system possess "magnetic" Yb [4], with the exception of YbCu_5 . This compound forms in the CaCu_5 hexagonal structure, and here Yb acts as a divalent alkaline earth. It is interesting, as an aside, that one of the largest known γ 's for a Yb material occurs in the compound $\text{YbCu}_{4.5}$ [5] whose structure is uncertain at present. We show our low-temperature specific-heat data for this material in fig. 4.

Substituting Ag, Pd and Au for one of the Cu's in YbCu_5 leads to formation of the C15_b structure. The Au and Pd compounds order magnetically below 1 K. The compound YbAgCu_4 does not order magnetically and has $\gamma = 245 \text{ mJ/mol Yb K}^2$ [6], at the edge of heavy-electron behavior.

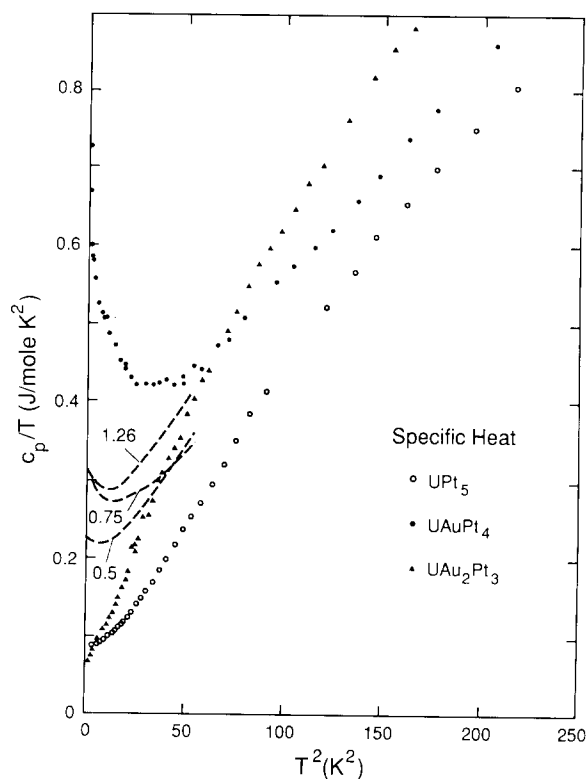


Fig. 3. Comparison of the low temperature specific heats of UPt_5 and $\text{UAu}_x\text{Pt}_{5-x}$.

The properties of this material are very similar to those of YbCuAl , and it is, in a number of ways, a cleaner material for study. Relatively few Yb-materials with large γ are known as yet.

3.2. CaCu_5 -structure

The CaCu_5 -structure is simple hexagonal with one formula unit per unit cell. The first coordination polyhedron of Ca contains 20 atoms, two of which are Ca, separated by the hexagonal c -axis spacing. The Cu-atoms occupy two inequivalent positions, a two-fold and a three-fold position. CeRh_3B_2 , a ferromagnet with $t_c = 112 \text{ K}$ has this structure [7].

Both CeCu_5 and CeZn_5 have this structure also. CeZn_3Cu_2 is also found in it, and it is known that both CeCu_5 and CeZn_3Cu_2 order magnetically near 5 K with low residual γ 's [8]. What is interesting is that Al substitution to form CeAlCu_4 and $\text{CeAlZn}_2\text{Cu}_2$ leads to very large γ 's with suppression of magnetic order (fig. 5). A very

similar set of results has been obtained with Ga substitution instead of Al in CeCu_5 , showing a very large peak near 0.5 K in γ of 3.4 mJ/mol Ce K^2 [9]. Below this temperature, γ decreases by about a factor two. This decrease of γ below 1 K without apparent accompanying phase transition is a common feature of many heavy-electron systems.

No definitive explanation exists for the spectacular increase of γ in these CeCu_5 -derived materials. It appears that T_K must be very low in this system and that the magnetic interactions are surprisingly sensitive to impurities, given the generally robust nature of magnetic interactions in the presence of impurities. There are other such sensitive systems – both U_2Zn_{17} [10] and UCu_5 [11] have been found with easily destroyed magnetic order. At least for UCu_5 , this sensitivity might be traced to the kind of underlying frustration discussed above.

3.3. Other structures

Heavy-electron behavior has been investigated recently in a number of other materials. The tetragonal compound CePtSi has been found to show both some kind of magnetic order near 3 K and a γ below 1 K of 840 mJ/mol Ce K^2 [12]. Shelton et al. [13] have also worked on this material. Sereni et al. [14] have found the extremely large $\gamma = 3.9$ mJ/mol Ce K^2 in the cubic CePd_3B . In this Cu_3Au -type material, B has apparently gone into the body center position.

We also mention here that high γ 's and very incompletely understood behavior have been found

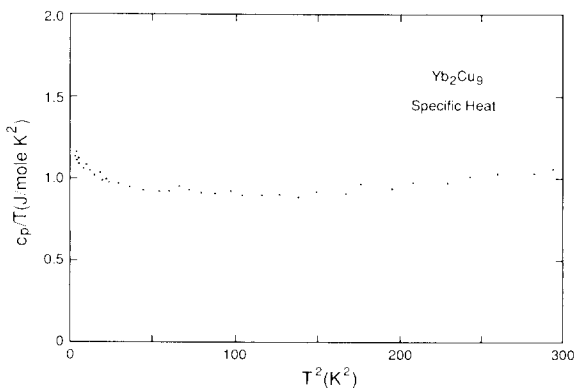


Fig. 4. Low temperature specific heat of $\text{YbCu}_{4.5}$.

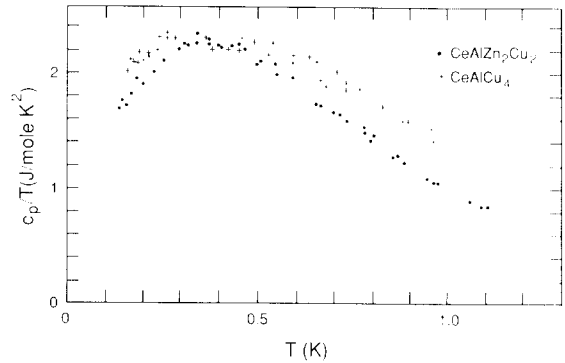


Fig. 5. Comparison of the low temperature specific heats of CeAlCu_4 and $\text{CeAlZn}_2\text{Cu}_2$.

in some of the Remeika phases $\text{Ce}_3\text{T}_4\text{Sn}_{13}$, T being a transition metal [15] and in rocksalt structure Yb-monopnictides [16].

3.4. Unusual materials

There are a few examples of materials that appear to fall outside the usual categories for describing Ce and U materials. One example is the $\text{RFe}_4\text{P}_{12}$ rare earth compounds studied by Meisner and co-workers in a series of papers [17]. While the La material is superconducting at 4.08 K, the Ce compound appears to be a small gap semiconductor. The lattice constant of the Ce compound is substantially lower than that of the La and Pr neighbors. This suggests that the Ce is in a state closer to Ce^{4+} , and magnetic susceptibility measurements find a much smaller Curie-Weiss constant than expected, corresponding to 2.7% of Ce^{3+} . What is surprising here is that this valence change makes the compound semiconducting. The Th analogue does not appear to be a superconductor or a semiconductor. Specific-heat measurements on the Ce compound find a very low value for the electronic term indicating a very small density of electronic states.

Perhaps related to this is the work of Palstra on the cubic compound UNiSn and related materials [18]. The structure here is the same as that found for the so-called half-metallic ferromagnets, typified by MnNiSb . The La analogue is metallic, the Th analogue to UNiSn has similar, semiconducting-type resistivity characteristic. Some kind of magnetic order occurs in UNiSn below 47 K. Low-temperature specific heat measurements find

$\gamma = 28 \text{ mJ/mol K}^2$, a very large value in view of the electrical resistivity behavior. The suggestion is that electronic correlations must be very large here.

A third set of compounds following this pattern have the general formula $R_3\text{Bi}_4\text{Pt}_3$. These are cubic, filled up Th_3P_4 -type structures, first studied by Dwight [19]. In this case the La and Pr examples are metallic, the Ce compound semiconducting. Additionally, the Ce lattice parameter lies between those of the La and Pr compounds, and the high temperature magnetic susceptibility has a Curie–Weiss behavior corresponding to $2.37\mu_B$, nearly the full moment for Ce^{3+} . There are also a large number of U analogues which can be formed in this structure. The question here is how, again, does this semiconductor-type behavior arise? So far, no low-temperature specific heat measurements have been performed, and the departures from Curie–Weiss behavior below 40 K have also not been examined carefully.

It is possible that electronic correlations are important in the properties of all these above materials, and that they represent an unusual border region to the more usual heavy-electron physics and in which charge fluctuations are important. Much more experiment is needed to address these materials.

4. Conclusion

Our aim has been to point out that more Ce heavy-electron materials exist than is generally realized. Certain crystal structures appear to favor the formation of the heavy-electron ground state and for these we suggest that the effective magnetic interactions are small. Chemical substitutions are in a number of cases very effective in suppressing magnetic order, and one strategy for seeking new, atomically ordered heavy-electron materials is via substitutions filling completely one site occupied by non-f elements in compounds possessing inequivalent non-f sites.

An interesting development in heavy-electron physics is the discovery of small moment ordering ($\approx 0.01\mu_B$) in a number of materials: URu_2Si_2 [20] and UPt_3 [21] are just two examples. Under what circumstances this occurs is not known, and it is not clear what relationship, if any, this kind

of ordering bears to larger moment orderings. Aspects of sample quality seem to be important for this ordering and a number of other low temperature properties of heavy-electron materials, and one clear direction for materials work in this field is in producing cleaner compounds.

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