CERIUM COMPOUNDS IN THE FASHION OF THE LIGHT ACTINIDES*

D. D. Koelling

Materials Science and Technology Division
Argonne National Laboratory, Argonne, Illinois   60439

June 1984

jmg

Manuscript submitted to the EPS Topical Conference on Electronic Structure and Properties of Rare Earth and Actinide Intermetallics, St. Polten, Austria, September 3-6, 1984.

DISCLAIMER

MASTER

Cerium Compounds in the Fashion of the Light Actinides

D. D. Koelling, Argonne National Laboratory, Argonne, Illinois 60439, U.S.A.

ABSTRACT

Researchers familiar with the light actinides easily recognize in cerium compounds a microcosm of the rich variety of properties seen in the light actinides. The parallelism seen between comparable cerium and actinide compounds strongly suggests that the same physical models are applicable. The most significant is the relative size of the f-orbital. Localization is generally tighter in Ce compounds than uranium compounds, making Ce roughly analogous to Np through Am. A way to see the actinide parallelism is to compare Hill plots. Compounds in the different regions of the plots (representing different physics) are isostructural compounds with the same companion (B) elements. The most common materials exhibiting a direct f-f interaction are the cubic Laves compounds. Accordingly, we have determined the band structures of $CeRu_2$, $CeRh_2$, $CeIr_2$, $CeOs_2$, and $CeNi_2$. Compounds illustrative of the interaction of f-orbitals with "ligand" orbitals are the Cu_3Au structured materials. Materials calculated in this class are $CeRh_3$, $CePd_3$, and $CeSn_3$--the materials of much interest as "mixed valent". Although the focus is on the Ce compounds, calculations performed on uranium isomorphs are used to highlight the interesting physics.

The wide variety of unusual properties observed in Ce and its compounds are well known. Also well established is the fact that the interesting physics in these materials arises from the transition of the 4f orbital from itinerant electron behavior to the local atomic behavior characteristic of the heavier rare earths. This closely parallels the behavior of the light actinides which has been widely noted--especially by the researchers who started in the actinides. One of the objectives here is to further detail that parallel. The basic philosophy is that the Ce materials involve the same physics and offering an opportunity to extend the range of critical parameters which are experimentally accessible. Protactinium being an extremely inconvenient material, Ce is practically the only "single f" system available for study. This simplification is extremely useful to theoretical analysis. Although certainly not negligible, relativistic effects are much less extreme in Ce than they are in the actinides. The semi-relativistic approximation plus spin orbit coupling is a valid approximation for Ce where it is questionable for the actinides [1].

Being a 4f system with no core f states, Ce tends to be more local and sharper in its properties--comparable to the difference between the comparison of the 3d and 4d transition materials. It thus more clearly delineates the borderline character and highlights the breakdown of the ancillary approximations in the band structure techniques being used to study these materials. An excellent example is the analysis of the photoemission spectra also being presented at this conference [2]. Although a band structure is formally only valid for the ground state, an approximation that often works well is to evaluate excitation energies as differences in band energies. This is simply not applicable for the poorly screened peak in Ce and actinide materials. It

2

is, however, easier to deal with in the Ce systems. The understanding of the poorly screened peak answers the question of why band structure calculations do not find a level below the Fermi energy. It simply doesn't belong in the bands but is a property of the excitation. As in the actinides, Ce compounds exhibit very sharp f resonances above the Fermi energy with amplitude pulled out into a tail of density that extends below the Fermi energy. The appropriate number of f electrons are accomodated in the occupied portion of this tail. For Ce, this is always close to one in all the intermetallics studied. This will be demonstrated below by giving the partial wave f count for each of the materials studied. Another example of the breakdown of ancillary approximations occurs in the specific heat in which case the deviations from the approximate interpretation of the band results occur at thermal temperatures. In $CeSn_3$, there is a factor of seven difference between the band density of states and the measured electronic specific heat even though the Fermi surface is described correctly [3]. These effects also occur in the actinides although often in a more muted fashion.

An excellent way to emphasize the parallel between Ce and the light actinides is to use an actinide tool to organize the systematic behavior of the Ce compounds: the inter-ion spacing correlation known as a Hill plot. Hill identified local moment formation as an index of localization and superconductivity as its antithesis. A very quick, if somewhat imprecise, qualitative index then is created by using the transition temperatures. This is not perfect (as can be seen for $CeFe_2$ where the Fe moment drives the magnetism of the material) but it is an excellent start for an overview. Hill then plotted the transition temperatures as a function of inter-ion spacing under the assumption that there would be a critical seperation beyond which the f-

orbitals would not be able to interact effectively. This is, in fact, correct. Hill at that time also recognized that Ce would fit this analysis [4]. A useful addition to make to this logic is the correction for coordination number. Very simply, a weaker interaction can be as effective as a stronger one if it occurs more times. This can be incorporated into the scheme by using empirical metallurgical corrections [5] shifting to the effective spacing for the same interaction strength were there a full 12 nearest neghbors (CN12). The revised plot shown in Fig.1 includes this shift. The resultant critical spacing is seen to occur in the range of 3.6-3.7 ^{8}. Making the CN12 correction has shifted the crossover in the cubic Laves phases to roughly the same separation as γ-Ce which is between CeN and CeP. It is quite significant that the cubic Laves phase structured materials are the predominant examples in this region where direct f-f interactions are to be expected. This occurs as well in the light actinides. The diamond sublattice is particularly favorable to the interaction of the xyz type f-orbital. Based on these observations a series of calculations were performed for the two superconductors $CeCo_2$ (.951f) and $CeRu_2$ (1.01f); for $CeRh_2$ (1.07f) which has the same lattice constant as $CeRu_2$ but is not superconucting; for $CeNi_2$ (0.96f) which has a lattice constant almost a small as $CeCo_2$; and for $CeOs_2$ (1.04f) and $CeIr_2$ (1.03f) which closely approach the critical separation. Here we will take only two simple observations from the results [7]. Comparing the charge analysis of $CeRh_2$ with $CeRu_2$, the simple atomic prediction that one should find one more d electron on the Rh (7.11d) than the Ru (5.97d) is realized in the band calculations. On the other hand, comparing CeRu2 with LaRu2 (0.20f), the f charge increases by 0.8 electrons. This implies that the standard use of a La compound as a comparable system with no f character will fail in these

materials. The replacement of La with Ce has not pulled an f band down far enough to accomodate a full f electron and the remaining charge has gone into the primarily d bands.

The Hill correlation is perfect for small spacings--there are no magnetic systems unless there is an Fe or Ni present to drive it. As should be expected, the correlation is not perfect for the large spacings. The direct f-f interaction is not the only interaction that an f orbital can experience. In that region, there are a number of materials that show no magnetic ordering and even some (such as UBe_{13}) that are actually superconductors indicating that these alternate interactions can be quite effective. The nature of the companion atom is also a strong determining factor as can be seen from the fact that the same structures and B atoms are found for the non-local-moment systems. URh_3 [8] was the first actinide system for which de Haas-van Alphen data was obtained. $CeRh_3$(1.25f) is referred to as the tetravalent metal although it does have an f charge. In the series of compounds with group IV elements, dHvA data has been obtained for UGe_3 and USn_3 is almost a heavy Fermion system [9]. $CeSn_3$ (120f) has been characterized as a mixed valent system for which dHvA data has also been obtained [10]. The parallel is weaker for $CePd_3$ (1.34f) since crystal field levels have been observed for UPd_3. However, UPd_3 is not in the Cu_3Au structure. UPd_4 does exist in this structure and does not show local moment behavior. Comparing the results from these systems to those for $LaSn_3$ (0.20) and $LaPd_3$ (0.37f), one sees that there is almost precisely one more f charge in the Ce material than in the La material. Th occupation of the other partial waves is essentially identical for the comparable La and Ce material. In these materials the La compound is a much better, although not perfect, no-f state analog [3].

In these cases, the f levels are inserted into and hybridize with the the transition metal-like band structure with a detailed balance of one f electron being introduced into the system. This occurs through a combination of pulling the f-bands down onto the Fermi energy (stronger in $CePd_3$) and hybridizing the f orbitals into the other levels (very strong in $CeRh_3$).

References

[1] A.H. MacDonald, W.E. Pickett, and D.D. Koelling, J. Phys. C 13, 2675 (1980).

[2] M.R. Norman, D.D. Koelling, and A.J. Freeman, this conference.

[3] D.D. Koelling, Sol. St. Commun. 43, 247 (1982).

[4] H.H. Hill, Proc. 4th Int. Conf. on Plutonium 1970 and Other Actinides (W.N. Miner, ed) Nucl. Metallurg. 17, 2 (1970).

[5] W.B. Pearson, Handbook of Lattice Spacings and Structures of Metals, Pergamon (1958) p 21.

[6] A.T. Aldred, B. Dunlap, D.J. Lam, and I. Nowik, Phys. Rev. B 10, 1011 (1974); A.T. Aldred, D.J. Lam, A.R. Harvey, and B.D. Dunlap, Phys. Rev. B 11, 1169 (1975).

[7] D.D. Koelling, in Proc. of the NATO Advanced Study Institute on The Electronic Structure of Complex Systems, Plenum Press (in press). The charge analysis of a number of La and Ce materials is summarized in Table VIII.

[8] A.J. Arko, M.B. Brodsky, G.W. Crabtree, D. Karim, D.D. Koelling, and L.R. Windmiller, Phys. Rev. B 12, 4102 (1975). (Recent SCF calculations have provided a better description of the Fermi surface.)

[9] A.J. Arko and D.D. Koelling, Phys. Rev. B 17, 3104 (1978).

[10] W.R. Johanson, G.W. Crabtree, A.S. Edelstein, and O.D. McMasters, Phys. Rev. Lett. 46, 504 (1981).

Figure Caption

Fig. 1. Separation correlation (Hill plot) for Ce including the effect of the
number of nearest neighbors. Temperatures above and below the "zero"
axis are superconducting transition temperatures and magnetic order-
ing temperatures, respectively. Symbols on the lo · and right hand
borders actually represent values well outside the scale of the plot.

Cerium Separation Correlation
With Corrections to CN12