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Title

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Permalink

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Journal

Journal of Alloys and Compounds, 181(1-2)

ISSN

0925-8388

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Publication Date

1992-04-01

DOI

10.1016/0925-8388(92)90333-5

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Ce₃Bi₄Pt₃ and hybridization Gap physics

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Abstract

Basic thermodynamic and transport properties of Ce₃Bi₄Pt₃ are reviewed. Although the susceptibility displays a canonical mixed valence temperature dependence, the electrical resistance, thermoelectric power and specific heat are those associated with a small gap semiconductor in which the gap is due to hybridization of the renormalized f and conduction electrons. In addition to this, a surprising correlation between the magnetic susceptibility and the thermal expansion as well as a simple theoretical framework within which hybridization-gapped systems can be viewed are presented.

1. Introduction

A small number of rare earth and actinide compounds are known which unexpectedly behave as semiconductors with very small gaps, typically of order 100 K, where by “unexpectedly” we mean that neighboring f elements form metallic, isostructural compounds. Compounds of this type are known for uranium and the rare earths cerium, samarium, thulium and ytterbium (see Table 1). The f elements forming such compounds are exactly those elements which have unstable f configurations. Europium is expected to

TABLE 1
Rare earth and actinide compounds exhibiting gaps

Compound	Structure	Δ (K)	Reference
CeNiSn	ϵ -TiNiSn	3	[5]
CeRhSb	ϵ -TiNiSn	7	[6]
Ce ₃ Bi ₄ Pt ₃	Y ₃ Sb ₄ Au ₃	50	[2]
CeFe ₄ P ₁₂	LaFe ₄ P ₁₂	~1000	[7]
SmB ₆	CaB ₆	30	[8]
SmS	NaCl	300–3000	[9]
TmSe	NaCl	–	[10]
TmTe	NaCl	3300	[11]
YbB ₁₂	UB ₁₂	70	[12]
UFe ₄ P ₁₂	LaFe ₄ P ₁₂	170	[13]
U ₃ Sb ₄ Pt ₃	Y ₃ Sb ₄ Au ₃	200	[14, 15]
UNiSn	MgAgAs	1200	[16]
UPtSn	MgAgAs	3400	[16]
URhSn	MgAgAs	4400	[16]

appear in this list, but we are not aware of any known compounds in this category formed by it. It has long been argued [1] that the small gap arises from hybridization between conduction and *f* electrons in the situation where the electron count in the material is such that the lower hybridized band will be exactly filled and the upper one empty. We believe that this interpretation contains part of the physics of the situation and will present evidence, as others have, that the energy scale for the gap is a Kondo scale and discuss why this might be so. We will also show why it is plausible that such compounds are found in structures possessing large gap semiconductors which are nearly always cubic. This viewpoint provides a rationale for the search for further such materials. Our discussion will be made against the experimental background of $\text{Ce}_3\text{Bi}_4\text{Pt}_3$, a hybridization gap compound whose properties we have been investigating [2].

$\text{Ce}_3\text{Bi}_4\text{Pt}_3$ crystallizes in a filled-up variant of the cubic Th_3P_4 structure, a structure first reported by Dwight for $\text{Y}_3\text{Sb}_4\text{Au}_3$ [3]. The isostructural compounds of lanthanum and praseodymium are metallic, while $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ is seen to have a semiconducting-type temperature dependence of its electrical resistivity (Fig. 1). Corresponding to this difference in resistance behavior is a lattice parameter for the cerium compound which indicates that the valence of cerium is more than three (Fig. 1, inset). The Hall constant of $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ also shows a temperature dependence which can be characterized by a gap of 50 K, and the mobility derived from the Hall constant and resistivity is sharply temperature dependent at low temperature, becoming

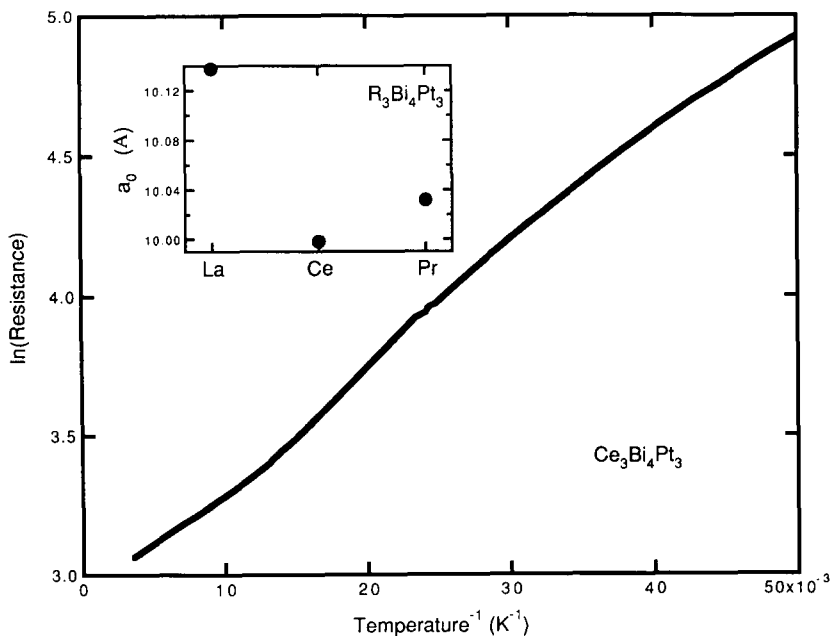


Fig. 1. Log(resistance) vs. inverse temperature for $\text{Ce}_3\text{Bi}_4\text{Pt}_3$. Inset: lattice parameter for $\text{R}_3\text{Bi}_4\text{Pt}_3$ ($\text{R} \equiv \text{La}, \text{Ce}, \text{Pr}$).

constant above 50 K, which is roughly the gap temperature (Fig. 2). We interpret this diminishing T dependence above about 50 K as indicating that the scattering of the carriers has “saturated”. We also note that the fit of the transport data to simple activated formulae is not especially good, but the data do clearly show the presence of a characteristic energy scale of 50 K in $\text{Ce}_3\text{Bi}_4\text{Pt}_3$.

The low temperature electronic specific heat coefficient γ of $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ is smaller than that of $\text{La}_3\text{Bi}_4\text{Pt}_3$ (Fig. 3), consistent with a gap in the electronic excitation spectrum of $\text{Ce}_3\text{Bi}_4\text{Pt}_3$. There is a variation of order a factor of 2 found in γ from sample to sample and a clear correlation exists between a larger rise in resistivity on cooling and a smaller γ , indicating that γ is most probably defect related. This relation can be further explored with deliberately introduced substitutions for cerium, and the effect of these substitutions on C_p is also shown in Fig. 3. It is seen that lanthanum substitutions generate a γ of approximately $600 \text{ mJ K}^{-2} (\text{mole La})^{-1}$ at low substitutions. This is the order of magnitude of γ for a typical Kondo impurity

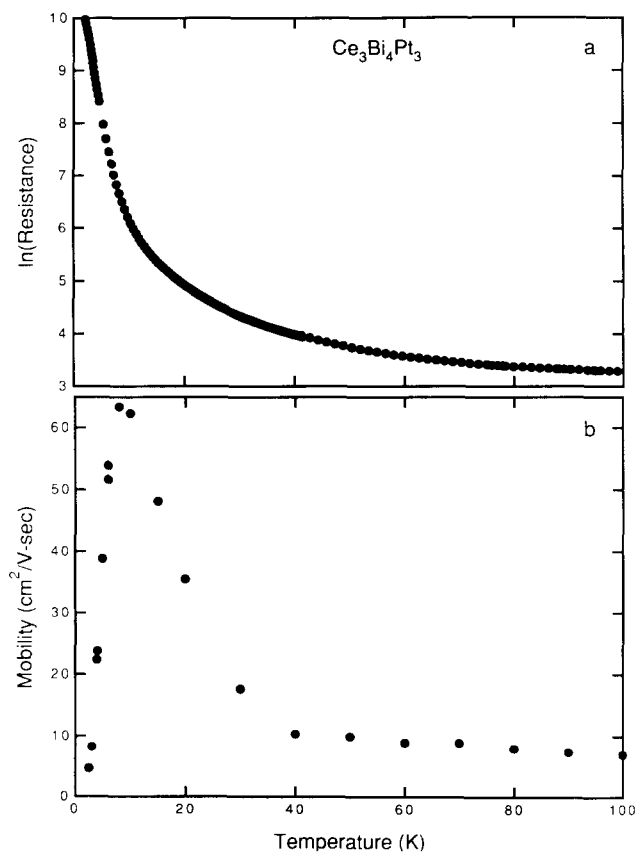


Fig. 2. Transport data for $\text{Ce}_3\text{Bi}_4\text{Pt}_3$: a, $\log(\text{resistance})$ vs. temperature; b, Hall mobility vs. temperature.

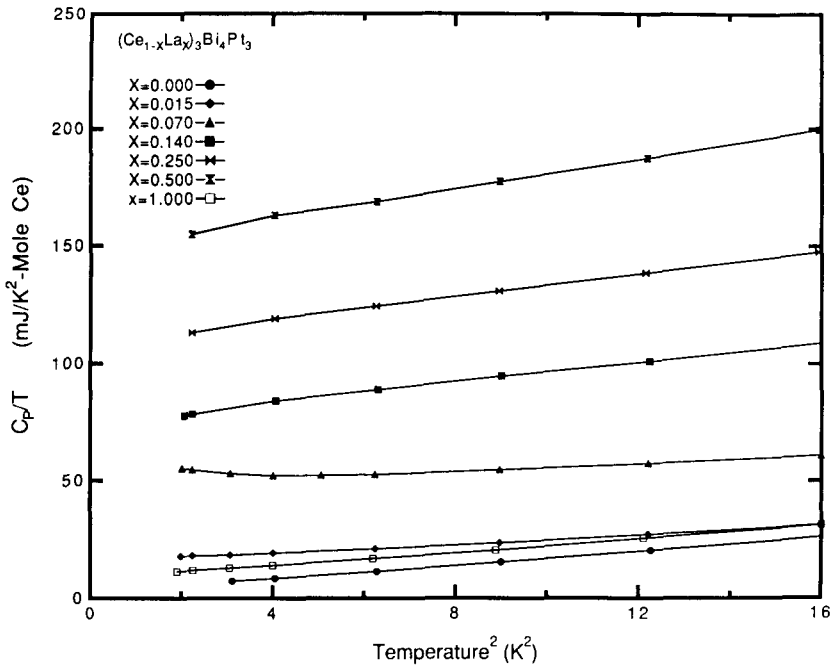


Fig. 3. C_p/T vs. T^2 for $(\text{Ce}_{1-x}\text{La}_x)_3\text{Bi}_4\text{Pt}_3$. Note that the units for the $x=1.0$ plot should be $\text{mJ K}^{-2} (\text{mole La})^{-1}$.

with $T_K \approx 10$ K and we interpret this as the specific heat γ of a Kondo “hole” generated by the lanthanum substitution.

The characteristic temperature scale is also evident in the temperature dependence of the magnetic susceptibility χ (Fig. 4, inset). The low temperature tail appears to be an “impurity” contribution with the same origin as the low temperature γ seen in the pure semiconducting material. The high temperature χ follows a Curie–Weiss-type behavior with slightly reduced moment, but the gap becomes evident below the peak near 80 K. The general form of this susceptibility can be fitted by taking the f^1 Ce configuration to lie 120 K above the ground state and we discuss below how this is consistent with general ideas about the hybridization gap ground state. In addition to this, inelastic neutron-scattering experiments [17] indicate that there is a gap in magnetic excitations at low temperatures. Analysis of the paramagnetic neutron-scattering function shows that the static susceptibility can be reproduced from the neutron data.

The deviation of the lattice constant of $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ from a value interpolated between the lanthanum and praseodymium analogues is an indication that charge fluctuations as well as spin fluctuations enter the physics of this small gap material. An unexpected relationship has been found between the susceptibility and lattice parameter temperature dependences (Fig. 4): a plot of χT vs. $\Delta a_0 = a_0(\text{La}_3\text{Bi}_4\text{Pt}_3) - a_0(\text{Ce}_3\text{Bi}_4\text{Pt}_3)$, with temperature as an implicit parameter, is linear except in the region of the lowest temperatures where

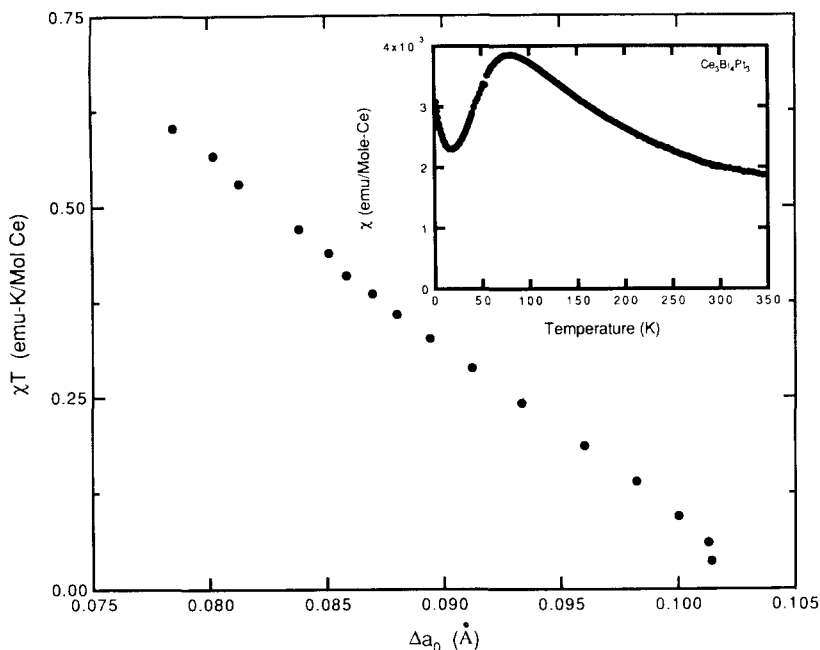


Fig. 4. χT vs. $\Delta a_0 = a_0(\text{La}_3\text{Bi}_4\text{Pt}_3) - a_0(\text{Ce}_3\text{Bi}_4\text{Pt}_3)$. Inset: χ vs. T for $\text{Ce}_3\text{Bi}_4\text{Pt}_3$.

the impurity Curie tail dominates the magnetic susceptibility. This presentation of the data was motivated by the observation that χT measures the effective moment squared of an isolated magnetic ion and that the low temperature magnetic susceptibility of $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ suggests a loss of magnetic moment. We do not have an explanation for the apparent accuracy of the linear relation and it does not in any obvious way follow from a Maxwell relation. Furthermore, it is interesting to note that a similar relationship holds for the metallic intermediate valent compound CeSn_3 , although the variations of χT and Δa_0 as functions of temperature are less dramatic in this case. This suggests that the relationship may be a general one in intermediate valence materials.

The large effects in specific heat induced by added impurities, coupled with the smallness of the gap in the pure material, suggest that the low temperature properties of the hybridization gap materials are Kondo derived. Loosely speaking, these gapped materials result from the development of a "Kondo" resonance in a material in which the resonance can exactly fill a Brillouin zone. This viewpoint is parallel to the simple picture in which an f level hybridizes with a conduction band and in which the low hybrid is just filled. More detailed many-body considerations show that it is not the f level but a renormalized f level which hybridizes with a conduction band at the Fermi level.

A special situation is required, however, for this hybridization to gap the entire Fermi surface: there can be only a single conduction band at the

Fermi surface for the renormalized f level to cut. If the f level cuts two bands, for example, a metal, not a semiconductor, results. Therefore materials which support the development of a hybridization gap need to have a particularly simple band structure near the Fermi level. We believe that this is the reason why almost all hybridization gap materials are cubic, since cubic materials have, very loosely speaking, the simplest band structures. Also, this is why there is so often found to be a semiconductor with “regular” gap in a compound isostructural to the hybridization gap compound, formed with an element replacing the f element which has the valence of the “anomalous” rare earth configuration, *e.g.* +4 for cerium and +2 for samarium. (For example, EuB_6 , in which europium is purely divalent, has a large gap, while isostructural SmB_6 manifests a much smaller hybridization gap.) The reason for the existence of these “regular” gap semiconductors is that again there is only one band being filled for the highest occupied states.

Our picture of the temperature evolution of the properties of the hybridization gap is the following. For $T > T_K$ the materials are dirty metals, the short electronic mean free path resulting from strong magnetic scattering of conduction electrons off the localized f electrons. In this temperature region the negative temperature coefficient of electrical resistivity results because the resistivity is larger than the Mooij [4] limit. When T drops below T_K , the Kondo resonance forms a filled zone and a gap of size order $k_B T_K$ separates the filled states from the lowest empty states. Owing to the highly correlated nature of the many-body ground state, the excitations from the low temperature ground state are only approximately described by the simple band picture of the hybridization gap. Part of the reason for this is that electronic correlations severely constrains the f level occupancy.

The place to look for further examples of hybridization gap materials is among semiconducting compounds formed with elements for which a rare earth with an unstable f shell can be substituted, with the “anomalous” valence of the rare earth being the same as the element for which it is substituting. What is surprising is that a number of structures are particularly prone to forming semiconductors with metallic elements. We mention in particular the “half-Heusler” MgAgAs and the orthorhombic $\epsilon\text{-TiNiSn}$ structures.

While the qualitative picture of the hybridization gap materials is quite simple, there is an important point to be made in connection with them: small energy scale electronic correlations in particular materials can alter the topology of the Fermi surface. This results in qualitatively different ground state properties, not just quantitative ones. It is here that important new physics of correlated materials may be found.

Acknowledgments

We acknowledge many useful discussions with G. Aeppli, S. Doniach and S. Trugmann. This work was performed under the auspices of the US Department of Energy.

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