

UC Irvine

UC Irvine Previously Published Works

Title

Kondo insulators

Permalink

<https://escholarship.org/uc/item/66z9201n>

Journal

Physica B Condensed Matter, 206(C)

ISSN

0921-4526

Authors

Fisk, Z
Sarraf, JL
Thompson, JD
[et al.](#)

Publication Date

1995-02-01

DOI

10.1016/0921-4526(94)00588-m

Copyright Information

This work is made available under the terms of a Creative Commons Attribution License, available at <https://creativecommons.org/licenses/by/4.0/>

Peer reviewed



ELSEVIER

Physica B 206 & 207 (1995) 798–803

PHYSICA B

Kondo insulators

Z. Fisk^{a,*}, J.L. Sarrao^a, J.D. Thompson^b, D. Mandrus^b, M.F. Hundley^b,
A. Miglori^b, B. Bucher^c, Z. Schlesinger^c, G. Aeppli^d, E. Bucher^d, J.F. DiTusa^d,
C.S. Oglesby^d, H-R. Ott^e, P.C. Canfield^f, S.E. Brown^g

^aNational High Magnetic Field Laboratory, 1800 E. Paul Dirac Drive, Tallahassee, FL 32306-4005, USA

^bLos Alamos National Laboratory, Mail Stop K764, Los Alamos, NM 87545, USA

^cIBM, T.J. Watson Research Center, Yorktown Heights, NY 10958, USA

^dAT&T Bell Laboratories, Murray Hill, NJ 07974, USA

^eLaboratorium für Festkörperphysik, ETH-Hönggerberg, 8093 Zürich, Switzerland

^fAmes Laboratory, Iowa State University, Ames, IA 50011, USA

^gDepartment of Physics, University of California, Los Angeles, CA 90024, USA

Abstract

The Kondo insulating materials present a particularly simple limiting case of the strongly correlated electron lattice problem, one occupied f-state interacting with a single half-filled conduction band. Experiment shows that the solution to this problem has some remarkably simple aspects. Optical conductivity data display the strong coupling nature of this physics.

The Kondo insulators are a group of small gap semiconductors in which the gap appears to derive from a weak hybridization between a localized f-level and a conduction band [1]. Another way to think about the gap formation is as a filling of the Brillouin zone by the Abrikosov–Suhl resonance resulting from the Kondo-like interaction of localized f- and conduction electrons. A number of the temperature-dependent physical properties of the Kondo insulators fit readily into this hybridization gap picture, but it proves difficult to account for all the macroscopic properties in detail using this model.

A simple argument suggests that these insulators present a well defined lattice problem in correlated electron physics. The 4f-compounds in this class always contain a 4f-element for which more than one valence state is possible (see Table 1). In addition, in almost every case there is an isostructural semiconductor known in which the 4f-element is replaced by a

non-4f-element having the anomalous valence state of the 4f-element replaced (e.g. +4 for Ce, +2 for Sm). Since the trivalent 4f-analogues of the insulators are metallic, we conclude that the hybridization in the Kondo insulators involves one occupied f-state crossing exactly one half-filled conduction band: crossing more than one band leads to a metallic state. Furthermore, there is a gap at the top of this conduction band, or below it, in the respective electron and hole cases (e.g. Ce or Sm). This condition ensures that the physics of the Kondo insulators follows from a particularly simple lattice model i.e. one occupied f-state interacting with a single half-filled conduction band. Nothing else is relevant. An interesting and related fact is that particular crystal structures favor the Kondo insulating ground state.

In this paper the typical properties of Kondo insulators are illustrated with the example of Ce₃Bi₄Pt₃, a cubic intermetallic whose lattice parameter deviates below the linear interpolation of those of the La and Pr analogue (inset, Fig. 1). Here this points to the possibility of intermediate valent Ce, and such lattice

* Corresponding author.

Table 1

Compound	Structure	Δ (K) ^a	Reference compound ^b	Reference
CeNiSn	ϵ -TiNiSn	3	TiNiSi	2
CeRhSb	ϵ -TiNiSn	7	TiNiSi	3
Ce ₃ Bi ₄ Pt ₃	Y ₃ Sb ₄ Au ₃	42	Th ₃ Sb ₄ Ni ₃	4
Ce ₃ Sb ₄ Pt ₃	Y ₃ Sb ₄ Au ₃	475	Th ₃ Sb ₄ Ni ₃	5
CeFe ₄ P ₁₂	LaFe ₄ P ₁₂	1500		6
SmB ₆	CaB ₆	27	SrB ₆	7
SmS	NaCl	300–3000	SrS	8
TmSe	NaCl	^c	SrS	9
TmTe	NaCl	3500	SrS	10
YbB ₁₂	UB ₁₂	62		11
FeSi	FeSi	300		12

^a Δ is the activation energy determined by transport measurements.

^bNon-f semiconducting analogue.

^cAn activation law does not fit the resistance behavior well.

parameter anomalies are common for Kondo insulators. The magnetic susceptibility (Fig. 1) follows a Curie–Weiss law above approximately 150 K with full Ce moment, but falls from a peak below 80 K to a $T \rightarrow 0$ K limiting value roughly half the peak value, when a sample-dependent Curie tail is removed. This tail has been shown by neutron scattering to be extrinsic. The electrical resistivity (Fig. 2(a)) increases when cooled below room temperature, three orders of magnitude in ‘good’ samples. An activation law was not followed, and the Hall mobility (Fig. 2(c)) was highly temperature-dependent, falling rapidly to a low, temperature independent value above about 40 K. The Hall number (Fig. 2(b)) is negative and

activated in the low temperature range with an activation energy of 40 K, where the sample-dependent extrinsic part below 15 K has been ignored.

The low temperature specific heat γ is found to be sample-dependent for Ce₃Bi₄Pt₃, but generally a factor of several smaller than that of La₃Bi₄Pt₃, for which $\gamma = 10$ mJ/mol-La K². Studies of Ce- and Pt-substituted alloys of Ce₃Bi₄Pt₃ show that deliberately introducing carriers produces large γ , values typical of Kondo impurities in metals. It was noted that a sample which becomes truly insulating as $T \rightarrow 0$ K has so far not been prepared for any Kondo insulator. The finite measured γ values for the nominally stoichiometric compounds is consistent with Kondo-type defect states with characteristic temperature of order the gap temperature.

Inelastic neutron scattering experiments on polycrystalline Ce₃Bi₄Pt₃ show that a gap opens at low temperature, of width approximately 12 meV (Fig. 3). This is somewhat larger than the peak temperature seen in χ , but this latter peak would only be expected to be of order the gap temperature, not exactly equal to it. The measured transport gap is somewhat smaller than this (taken from the Hall data), even allowing for the usual factor of two in the transport expressions. However, the transport will measure the smallest gap in the system. Also, it was noted that a plot of χT versus the difference between the lattice parameter of La₃Bi₄Pt₃ and Ce₃Bi₄Pt₃ (δa_0) with T as an implicit parameter gives a straight line (Fig. 4(a)). Additionally, δa_0 fits a simple activation expression with $\Delta = 120$ K (Fig. 4(b)). This suggests that δa_0 measures the number of occupied f-states, as does χT for non-interacting moments, and that this charge effect has the same characteristic activation energy as seen in the

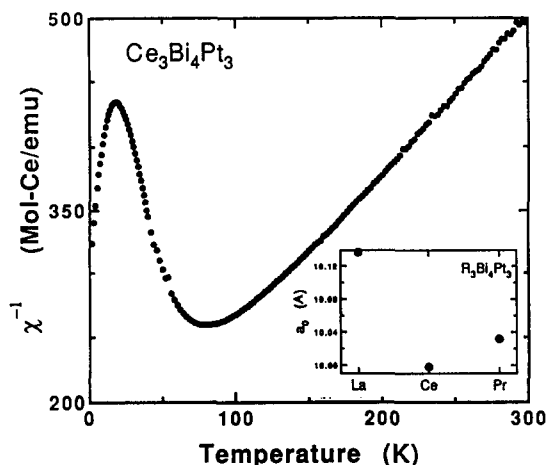


Fig. 1. Magnetic susceptibility of Ce₃Bi₄Pt₃. Inset shows the deviation from the linear interpolation of the R₃Bi₄Pt₃ lattice constant for R = Ce [4].

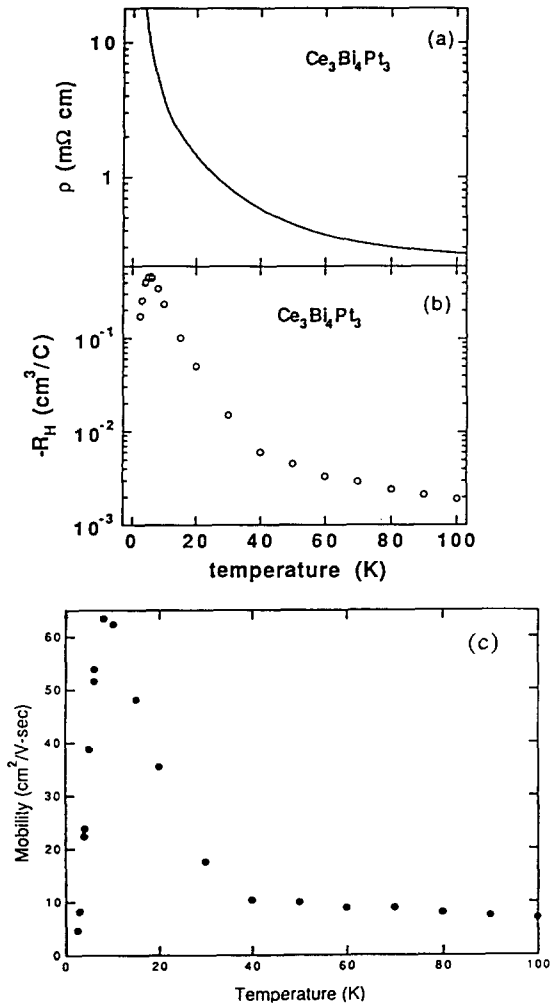


Fig. 2. Temperature dependence of electrical resistivity, Hall number, and Hall mobility in $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ [4].

inelastic neutron measurements of the spin gap. That the moments are non-interacting implies that $\chi'(q)$ should be q -independent. This has been shown to be the case, within certain limits, in CeNiSn (Fig. 3) as well as the transition metal compound FeSi [16], believed to be in this class of materials. Careful specific heat measurements on $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ and $\text{La}_3\text{Bi}_4\text{Pt}_3$ show that the full entropy of $R \ln 6$ J/mol-Ce K expected for the $J = 5/2$ Hund's Rule ground state of f^1 Ce is essentially recovered by $T = 200$ K, giving good reason to regard the temperature evolution of the properties of these materials as involving the full appearance of localized f^1 Ce moments.

It is interesting to examine the extent to which the

temperature dependent properties of $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ and other Kondo insulators can be modeled with a simple semiconducting gap. Towards this end optical conductivity measurements have been carried out over a wide energy range. In Fig. 5 we show the temperature dependent optical conductivity data, as well as the integrated spectral weight as a function of frequency and temperature. There are two essential points here. The first is that the rather large optical gap (350 cm^{-1}) fills in by 200 K, much lower than the gap energy. And second, the optical sum rule is only satisfied by integration out to energies an order of magnitude larger than the gap. This substantial rearrangement in energy of the spectral weight points out the strong coupling nature of the problem. Essentially the same features have been observed in the optical conductivity of FeSi (Fig. 6). Recent measurements by Degiorgi et al. [19] found effects smaller in magnitude, but the sample measured there differs both in the magnitude of the observed gap and the residual resistivity.

Further interesting effects are seen in the optical conductivity data of mixed valent and metallic CePd_3 . The data (Fig. 7) are remarkably similar to that for $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ and FeSi , except for the renormalized Drude piece at very low energies left at low temperatures. This compound shows a pseudo-gap opening at low temperature, with shift in spectral weight to energies considerably higher than the gap. This material may be classed as a failed Kondo insulator, as speculated earlier by Kasuya [21]. Here again, we see the almost mean field relation between the gap magnitude and the temperature at which the gap is no longer visible in the optical conductivity.

A comparison, isostructural compound to CePd_3 is CeSn_3 , a mixed valent metal. What we see in the optical spectra of this compound (Fig. 8) the formation of a pseudo-gap at low temperature, but the spectral weight in this case is redistributed only to energies near the gap frequency.

The tentative conclusion to be drawn from these optical measurements is that the Kondo insulators show dramatic, strong coupling features not present or diminished when one dilutes away from the one conduction electron per occupied f -state limit. Additionally, simple semiconductor statistics do not trivially produce the gap filling with temperatures as observed. The temperature-dependent properties of these insulators seem more easily described as the thermally-induced appearance of localized f -electrons, each thermal excitation yielding one conduction electron. At sufficient excitation, a dirty metal results, dirty in the sense that each local moment scatters

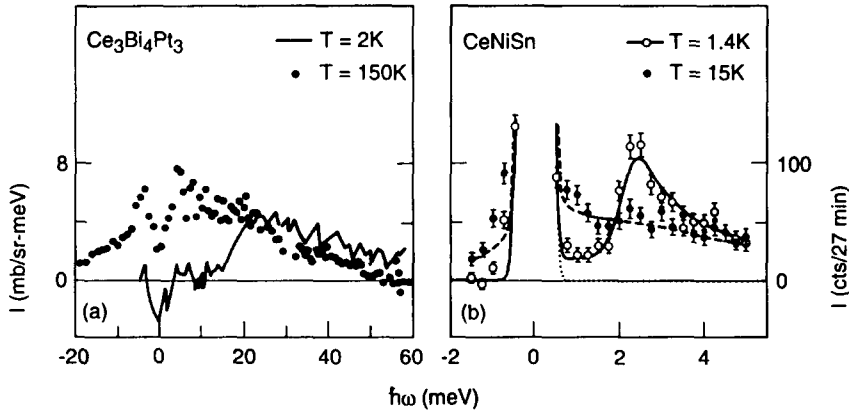


Fig. 3. Neutron scattering response $S(Q, \omega)$ as a function of energy transfer for polycrystalline $Ce_3Bi_4Pt_3$ and single crystal $CeNiSn$. The scattering at $\hbar\omega = 0$ for $CeNiSn$ is incoherent. This contribution has been subtracted from the $Ce_3Bi_4Pt_3$ data [13,14].

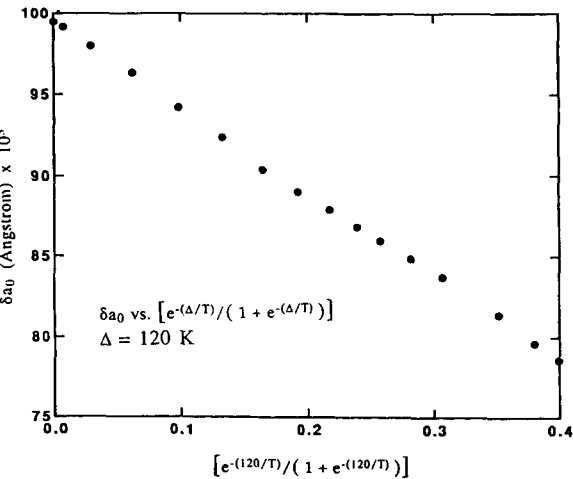
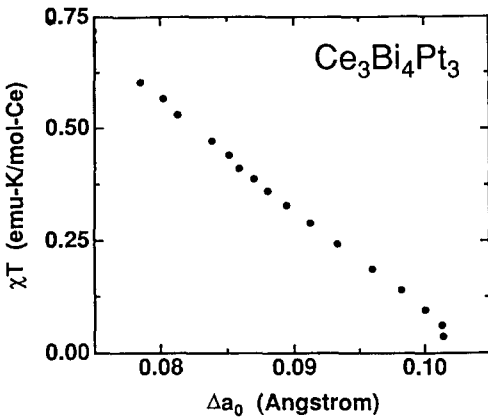


Fig. 4. χT versus δa_0 , and δa_0 plotted against a simple activated form with $\Delta = 120$ K [15].

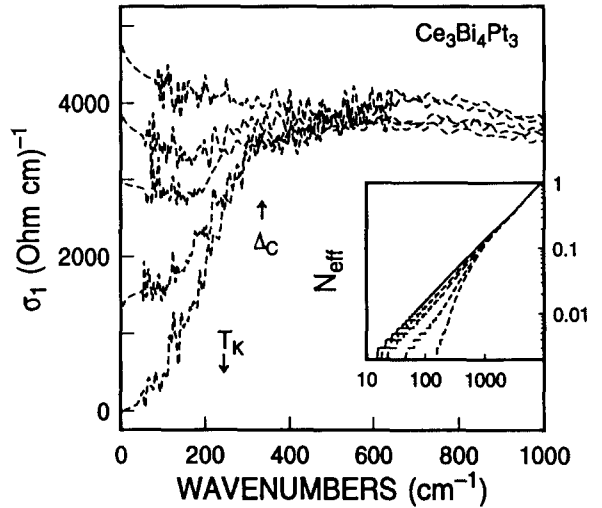


Fig. 5. The optical conductivity of $Ce_3Bi_4Pt_3$ for different temperatures (from below: 25, 50, 75, 100, and 300 K). A gap is opening below 100 K; the prominent feature at Δ_c seems to be temperature independent. The inset shows the effective carrier density derived from this data [17].

conduction electrons at the unitary limit. The gap disappears when a sufficient number of excitations is present.

The apparent appearance of local moments with increasing temperature is interesting in the context of mixed valence and Luttinger's theorem as well [22]. A lot of work remains to be done to both provide an acceptable description theoretically, as well as a clean picture experimentally. Much more work is needed in

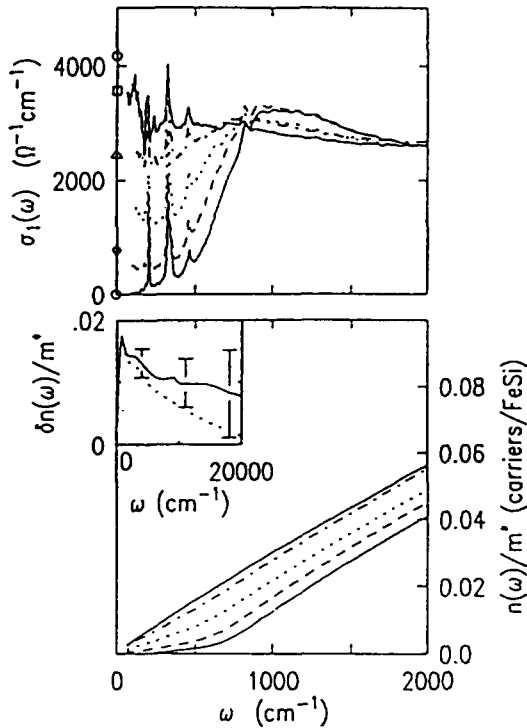


Fig. 6. The optical conductivity and effective carrier density of FeSi for different temperatures ($T=20$ (solid), 100 (dashed), 150 (dotted), 200 (dot-dashed), and 250 K (solid)). The inset of the lower panel shows the difference between $n(\omega)/m^*$ at 250 and at 20 K (solid curve). The dotted curve shows the effect on $n(\omega)/m^*$ of shifting the 20 K reflectivity data by +0.5% [18].

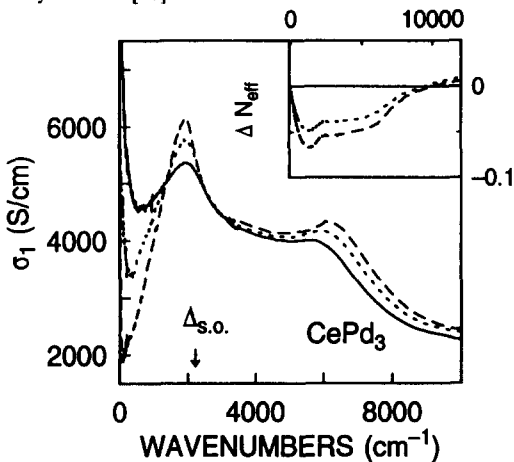


Fig. 7. Optical conductivity of CePd₃ at 250 (solid), 150 (dotted), and 25 K (dashed). Spectral weight below 1000 cm⁻¹ shifts to higher energy. The inset shows ΔN_{eff} , the difference between the effective carrier density N_{eff} (per formula unit) at a temperature T and at 250 K, for $T=150$ and 25 K [20].

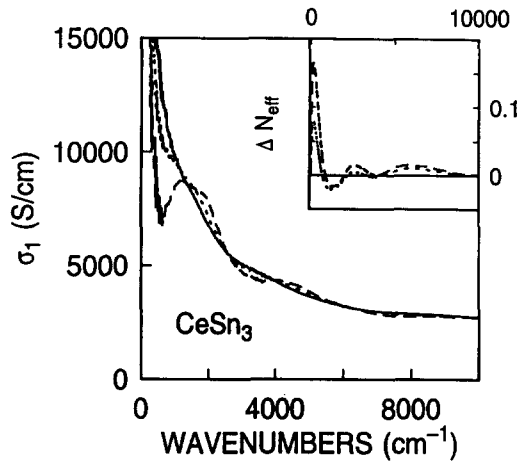


Fig. 8. Optical conductivity of CeSn₃ at 250 (solid), 150 (dotted), and 25 K (dashed). Below 1000 cm⁻¹ spectral weight shifts to lower energy as temperature decreases. The inset shows ΔN_{eff} , the difference between the effective carrier density N_{eff} (per formula unit) at a temperature T and at 250 K, for $T=150$ and 25 K [20].

the preparation of good materials, particularly in view of the difficulties associated with extricating intrinsic from extrinsic behavior, but this is inherent in work on new materials. And there is much promise here. This strong coupling problem covers two extremes of correlated electron behavior, semiconductivity and localized moments, and appears to be a well defined, simply posed theoretical question, parts of whose solution are remarkably simple.

References

- [1] G. Aeppli and Z. Fisk, *Comm. Condens. Matter Phys.* 16 (1992) 155; G. Aeppli et al., in: *Proc. Los Alamos Symp. on Correlated Electron Systems*, ed. K. Bedell (Addison-Wesley, New York) in press.
- [2] T. Takabatake et al., *Jpn. J. Appl. Phys. Suppl.* 26 (1987) 547; *Phys. Rev. B* 41 (1990) 9607.
- [3] S.K. Malik et al., *Phys. Rev. B* 43 (1991) 6277.
- [4] M.F. Hundley et al., *Phys. Rev. B* 42 (1990) 6842.
- [5] M. Kasaya et al., *Solid State Commun.* 78 (1991) 797.
- [6] M.S. Torikachvili et al., in: *Proc. LT-17*, ed. H. Eckern (North-Holland, Amsterdam, 1984) p. 875.
- [7] J.W. Allen et al., *J. Appl. Phys.* 49 (1978) 2078.
- [8] A. Jayaraman et al., *Phys. Rev. B* 11 (1975) 2783.
- [9] P. Haen et al., *Phys. Rev. Lett.* 43 (1979) 304.
- [10] H. Boppart, *J. Magn. Magn. Mater.* 47–48 (1985) 436.

- [11] M. Kasaya et al., *J. Magn. Magn. Mater.* 47–48 (1985) 429.
- [12] S. Föex, *J. Phys. Radium* 9 (1938) 37; V. Jaccarino et al., *Phys. Rev.* 160 (1967) 476.
- [13] A. Severing et al., *Phys. Rev. B* 44 (1991) 6832.
- [14] T. Mason et al., *Phys. Rev. Lett.* 69 (1992) 490.
- [15] Z. Fisk et al., *J. Alloys Comp.* 181 (1992) 369.
- [16] G. Shirane et al., *Phys. Rev. Lett.* 59 (1987) 351.
- [17] B. Bucher et al., *Phys. Rev. Lett* 72 (1994) 522.
- [18] Z. Schlesinger et al., *Phys. Rev. Lett.* 71 (1993) 1748.
- [19] L. Degiorgi, *Physica B* 206 & 207 (1995) 441, 810.
- [20] B. Bucher et al., *Phys. Rev. Lett.* (1994) submitted.
- [21] T. Kasuya et al., *J. Less-Common Met.* 127 (1987) 337.
- [22] C.M. Varma, *Physica B*, presented at SCES'94, Amsterdam, 15–18 August 1994 (unpublished).