

THERMODYNAMICS AND TRANSPORT IN $Ce_3Bi_4Pt_3$ AND RELATED MATERIALS

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INTRODUCTION

The interplay between electronic and magnetic correlations in certain 4f and 5f intermetallic compounds has been shown to lead to novel ground state properties, including strongly renormalized effective electron masses, homogeneous mixed valence of the f-configuration and unconventional superconductivity. Whereas the vast majority of these compounds are metallic at low temperatures, a few examples, such as SmB_6 (Ref. 2), SmS (Ref. 3), and YbB_{12} (Ref. 4), have been known for some time to be small-gap semiconductors, with gaps of order 100K. Within the past two or three years several new examples have been discovered, notably in Ce_5-8 and U_9 compounds, suggesting that small-gap semiconductors may be a general consequence of strongly interacting electrons. With very few exceptions, the crystal structures of these materials are cubic which, as will be argued, is favorable for the appearance of a small gap in the electronic spectrum. Further common features are temperature variations in the cubic lattice parameter, in magnetic susceptibility and in L-edge absorption spectra that are consistent with an unstable f-configuration arising from hybridization between f and ligand electrons. The extent to which the physics of these small-gap semiconductors is similar to metals with otherwise similar properties remains an outstanding question but their analogous behavior to Kondo-lattice metals has led to the terminology Kondo insulators.^{10,11} In the following we review transport and thermodynamic properties of the small-gap semiconductor $Ce_3Bi_4Pt_3$ and discuss them in relation to what is known about other Kondo insulators and metals.

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Ce₃Bi₄Pt₃

Figure 1 compares the temperature-dependent resistivity $\rho(T)$ of single crystal Ce₃Bi₄Pt₃, La₃Bi₄Pt₃ and Pr₃Bi₄Pt₃. Whereas $\rho(T)$ for the isostructural La and Pr analogues is typical of dirty intermetallic compounds, that of the Ce compound increases strongly with decreasing temperature. An Arrhenius plot of the Ce₃Bi₄Pt₃ data shows activated behavior above approximately 50K, with an activation energy $\Delta=50$ K or gap energy $E_g = 2\Delta$ of about 100K, if the Fermi level lies in the center of the gap.* Below 50K, $\rho(T)$ increases less rapidly than exponentially, with the deviation from activated behavior depending on sample quality. For crystals prepared with higher purity (Ames Laboratory) Ce, the Arrhenius plot remains activated to lower temperatures but the magnitude of Δ is relatively insensitive to these effects, suggesting that small amounts (of order 0.1%) of impurities introduce electronic states in the gapped region. A crude measure of sample quality, therefore, is the resistivity ratio $\rho(2K)/\rho(300K)$ which approaches 1000 in the "best" crystals. Even in these, one should consider the low-temperature transport to be influenced by extrinsic effects.

Similar conclusions are drawn from Hall-coefficient RH and thermoelectric power measurements¹² which show above about 50K temperature dependences characteristic of an electronic gap $E_g=100$ K, but at lower temperatures both are dominated by parallel conduction channels arising from impurity states in the gap. Above the extrinsic carrier-dominated regime the Hall mobility,¹³ $\mu=RH/\rho$, saturates to a small, temperature-independent value of 10 cm²/V-sec, suggesting strong scattering of carriers with enhanced effective mass.

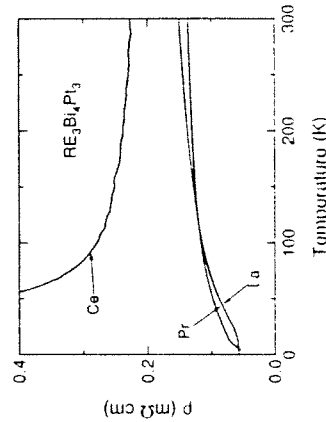


Fig. 1 Resistivity, plotted on a linear scale, as a function of temperature for single crystals of Ce₃Bi₄Pt₃, La₃Bi₄Pt₃ and Pr₃Bi₄Pt₃. Above approximately 100K, the resistivity of Ce₃Bi₄Pt₃ begins to increase at a rate $\partial\rho/\partial T$ comparable to what is seen in La and Pr analogues below 300K. Measurements to 40 mK show no evidence for a phase transition in Ce₃Bi₄Pt₃.

As to be expected for a small-gap semiconductor, the electronic contribution to the specific heat γ of Ce₃Bi₄Pt₃ is small, $\gamma = 3$ mJ/mole-Ce-K², a value about one-third that of La₃Bi₄Pt₃. That a measurable contribution is found at all reflects the presence of extrinsic carriers. Application of a 10T-magnetic field has no effect on the specific heat in the temperature interval $1.5 < T < 20$ K of the measurements. This result contrasts to observations¹⁴ on the orthorhombic, small-gap ($\Delta = 5$ K) semiconductor CeNiSn in which C/T at low temperatures increases by about a factor of two when an 8T field is applied along the a-axis. This could arise because the ratio of field-strength to gap-energy differs substantially in these two experiments and/or from the anisotropic nature of the energy gap in CeNiSn. Magnetoresistance behavior in these two materials will be discussed below.

Evidence for mixed-valence nature of the 4f configuration is found in the magnetic susceptibility χ and thermal expansion of Ce₃Bi₄Pt₃. Figure 2 shows χ versus temperature for a Ce₃Bi₄Pt₃ crystal produced from Ames Laboratory Ce. The temperature dependence is Curie-Weiss above ~ 100 K, with an effective moment $\mu_{eff} = 2.42 \mu_B/\text{Ce}$ and a paramagnetic $\Theta_p = 125$ K. The broad peak in χ , centered at $T_K = 80$ K, is characteristic of metallic mixed-valence compounds having a Kondo temperature $T_K \approx (3-4)T_C = 240-320$ K (Ref. 6). In contrast to earlier measurements⁶ on samples prepared with less-pure (99.9%) Ce that showed a pronounced "Curie-tail" at low temperatures, the data of Fig. 2 approach a constant value $\chi(0) = 2.3 \times 10^{-3}$ emu/moleCe. This large $\chi(0)$ most definitely is not Pauli-like and possibly arises from an unquenched orbital contribution of the 4f moment that gives a Van Vleck-type susceptibility with characteristic energy on the order of Δ .

Inelastic neutron scattering measurements¹⁵ on powdered single crystals reproduce the temperature dependence of the static susceptibility, as also shown in Fig. 2. What is

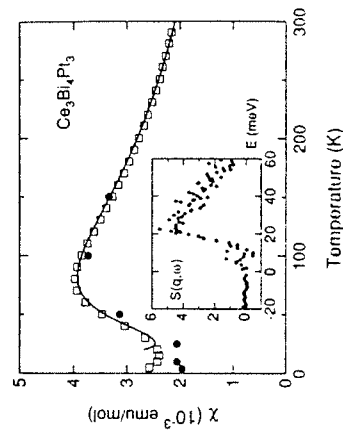


Fig. 2 Magnetic susceptibility χ versus temperature for Ce₃Bi₄Pt₃ measured in a field of 1T. Open circles denote χ obtained from the neutron scattering function $S(Q, \omega)$. The solid line is $\chi(T)$ calculated as described in the text. Inset shows the magnetic contribution to $S(Q, \omega)$ versus energy transfer at $T=2$ K for an incident neutron energy of 69 meV. A gap in the spin-spin correlation function of 12 meV is apparent.

not apparent in Fig. 2 but is revealed by neutron scattering is that below approximately 50K a well-defined gap in the spin-spin correlation function develops. (See Fig. 2 inset.) At 2K, this gap is 12 meV (140K), a value comparable to E_g inferred from transport measurements and below which magnetic intensity is zero. The gap remains well-defined to 25K but above 50K magnetic scattering at small energy transfer develops rapidly with increasing T. By 150K, the magnetic scattering is quasi-elastic like, consistent with a TK inferred from susceptibility measurements. Similar conclusions are drawn from NQR studies.¹⁶ Evidence for a spin-gap has also been reported in the small-gap semiconductor CeNiSn¹⁷ and in the mixed-valent metal YbAl₃ (Ref. 18).

Temperature variations in the cubic lattice parameters a_0 of Ce₃Bi₄Pt₃ and La₃Bi₄Pt₃ are given in Fig. 3(a). An anomalous decrease in a_0 is seen below 100K for Ce₃Bi₄Pt₃, which for metallic Ce compounds would be argued as an indication of admixed 4f₀ and 4f₁ configurations. (Preliminary L_{III}-edge x-ray absorption experiments on Ce₃Bi₄Pt₃ indicate an f-occupancy $n_f \approx 0.9$).¹⁹ The 4f-contribution to the volume-thermal expansion

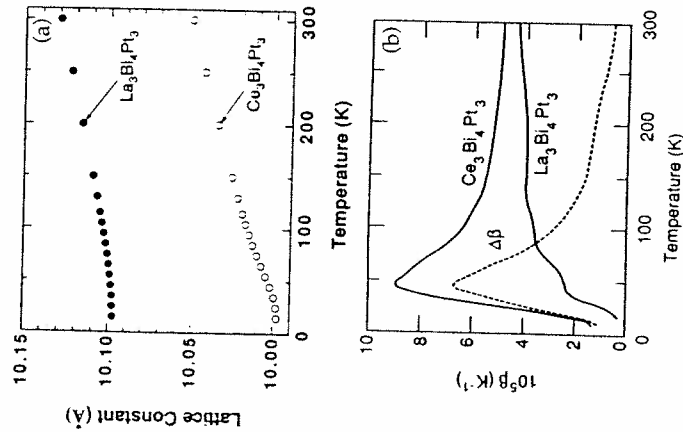


Fig. 3. (a) Cubic lattice parameter, determined by Rietveld analysis of neutron-diffraction spectra, of Ce₃Bi₄Pt₃ and La₃Bi₄Pt₃ as a function of temperature. (b) Volume-thermal expansion coefficient for both compounds calculated from the data in (a) and their difference $\Delta\beta(T)$, which gives the 4f-derived contribution to the thermal expansion.

is displayed more obviously in Fig. 3(b) where the volume thermal expansion coefficient $\beta = 3\partial(a_0)/\partial T$ of both compounds and their difference $\Delta\beta = \beta_{\text{Ce}} - \beta_{\text{La}}$ are plotted as a function of temperature. The difference $\Delta\beta$ peaks at $T_{\Delta\beta} \approx 50\text{K}$. By Maxwell's relations, then, the pressure derivative of the 4f entropy also peaks at $T_{\Delta\beta}$. Similar measurements²⁰ performed with the samples subjected to an applied pressure of 17.7 kbar give $T_{\Delta\beta} \approx 85\text{K}$ and, from a comparison of the ambient and high pressure data for Ce₃Bi₄Pt₃, a $T \rightarrow 0$ bulk modulus of about 950 kbar. An analysis of these results yields a Grüneisen parameter $\Omega = 36$ comparable to that expected of a metallic-mixed valent compound with a T_K of 200-300K.

A remarkable observation¹³ is that the difference in lattice parameters Δa_0 between that of Ce₃Bi₄Pt₃ and La₃Bi₄Pt₃ is linear in the product χT , as shown in Fig. 4(a). In the absence of interactions, χT is just the volume density of moments contributing to the susceptibility. A linear fit to these data gives $\chi T = -27.31\Delta a_0 + 2.76$ (emu·K/mole·Ce). A second interesting observation[†] is that, as shown in Fig. 4(b), the function $1/(1 + \exp(\Delta/T))$ linearizes $\Delta a_0(T)$ to a good approximation. More precisely $\Delta a_0 = -0.529/(1 + \exp(120/T)) + 0.099$ (Å). We note that the numerator in the exponential is very close in

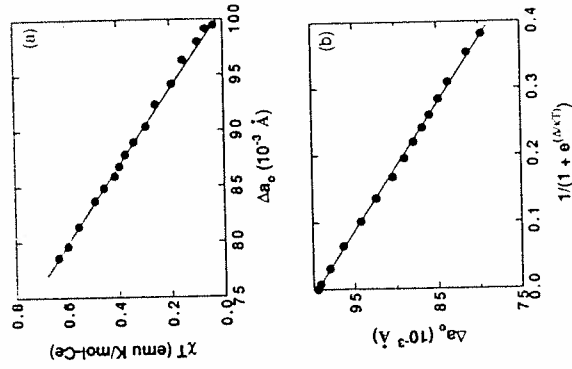


Fig. 4. (a) Product of static susceptibility times temperature versus the lattice-parameter difference $\Delta a_0 = a_0(\text{La}_3\text{Bi}_4\text{Pt}_3) - a_0(\text{Ce}_3\text{Bi}_4\text{Pt}_3)$, with temperature as the implicit variable. (b) Δa_0 versus $1/(1 + \exp(\Delta/T))$. A linear relationship is found for $\Delta/k_B \approx 120 \pm 5\text{K}$.

magnitude to the value of the gap in the spin-spin correlation function measured at low temperatures by inelastic neutron scattering¹⁵ and to the paramagnetic Θ_p found from fitting a Curie-Weiss form to the high-temperature susceptibility (Fig. 2). Together these two relationships allow the temperature-dependent susceptibility to be calculated directly, the results of which are shown in Fig. 2 as the solid line. The relatively good agreement between measured and calculated values of χ above ~ 30 K confirms consistency in the parameterizations of $\Delta_0(T)$; but perhaps more significant is that when $\chi(T)$ is viewed this way no Curie-Weiss Θ_p , i.e., no interactions in the conventional sense, is required to understand the temperature variations in χ at low T .²¹

To probe the ground state of $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ in more detail, the response of the electrical resistivity to applied magnetic fields and pressures has been measured. Fig. 5(a) shows the magnetoresistance $\Delta\rho/\rho = [\rho(H) - \rho(H=0)]/\rho(H=0)$ of $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ at selected temperatures. At low temperatures, $\Delta\rho/\rho$ is strongly negative at high fields but exhibits a weak positive contribution at low fields. (Preliminary measurements²² at 4K in fields to 50T find an approximately two-order-of-magnitude decrease in the resistivity, so that the sample is nearly metallized by a field comparable to Δ . Similar results have been reported²³ for CeNiSn with $H=11$ T parallel to the orthorhombic a-axis.) With increasing temperature,

the positive contribution dominates at all fields below 10T. An unusually large, positive magnetoresistance is also found in the non-magnetic analogue $\text{La}_3\text{Bi}_4\text{Pt}_3$ (Fig. 5(b)) that saturates at progressively lower fields with decreasing temperature and can be scaled to fit the positive $\Delta\rho/\rho$ in $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ (Ref. 24). Given the low mobility in $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ and comparable values of room-temperature resistivity in the Ce and La compounds, we believe this field and temperature dependence reflects the condition $\omega_c\tau \sim 1$ at about 1T where ω_c is the cyclotron frequency. Comparison of Figs. 5(a) and (b) then suggests that the room-temperature band structures of both materials are similar and that the 4f interaction with the common underlying electronics results in the appearance of the gap in $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ and its large negative $\Delta\rho/\rho$ at low temperatures.

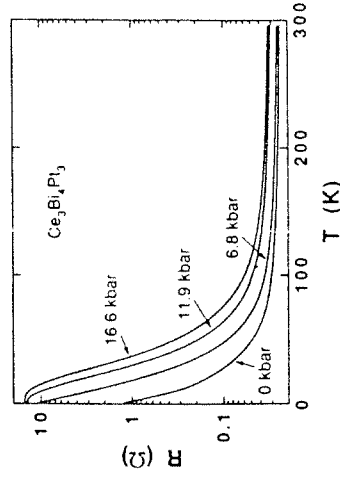


Fig. 6. Resistance as a function of temperature for $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ subject to various applied hydrostatic pressures.

From the linear relationship found in Fig. 4(b) and the observation²⁰ that at low temperatures Δ_0 increases with pressure, it is straightforward to show that $\partial\Delta/\partial P > 0$, if Δ in Fig. 4(b) is associated with the spin or charge gap. That is, decreasing the cell volume, which favors stronger admixture of the 4f configuration, should enhance the gap. Figure 6 gives resistance versus temperature measurements for $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ at pressures to over 16 kbar. These experiments were performed on an early sample in which $\rho(2\text{K})/\rho(300\text{K})$ was only 30. In spite of this, the data clearly show trends consistent with $\partial\Delta/\partial P > 0$. At the highest pressures, the low-temperature resistance saturates, most likely reflecting parallel conduction by impurity states in the gap. Depending on details of the analysis, we find that $\partial\rho/\partial P$ ranges from 0.05 to 0.16 kbar^{-1} consistent with the Grüneisen interpretation of the pressure-dependent thermal expansion.²⁰ This result contrasts to observations^{25,26} on SmB_6 and YbB_{12} in which pressure suppresses the electronic gap. In the case of SmB_6 , $\partial\rho/\partial P$ varies from -0.02 to about -0.03 kbar^{-1} depending on the sample. (The sign difference between $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ and SmB_6 in their logarithmic derivatives of Δ are reflected as well in sign differences in their 4f-derived thermal expansion.)^{20,27}

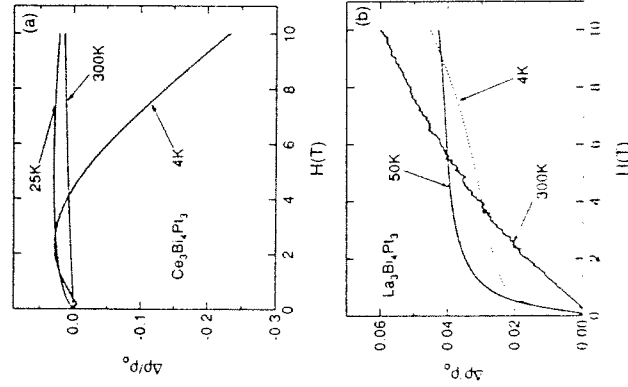


Fig. 5. Normalized magnetoresistance $\Delta\rho = [\rho(H) - \rho(H=0)]/\rho(H=0)$ as a function of magnetic field for (a) $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ and (b) $\text{La}_3\text{Bi}_4\text{Pt}_3$ at selected temperatures.

At pressures of 55 to 70 kbar the electronic gap in SmB_6 is closed and the temperature-dependent resistance becomes that of a typical Kondo-lattice metal.^{10,25} X-ray diffraction at room temperature indicates²⁸ the valence of Sm changes from 2.8 at $P=0$ to 2.9 at 60 kbar. Thus, with applied pressure the magnetic $4f^5$ configuration of Sm is favored over the $4f^6$ ($I=0$), leading to a decrease in charge hybridization and an approach to the Kondo-limit. Similar arguments apply to YbB_{12} . On the other hand, the $4f^0$ configuration in Ce is favored at high pressure and we expect a more strongly mixed-valent, less magnetic ground state. In these materials, then, Δ tracks the expected change²⁹ with pressure in charge/spin hybridization and not band filling because in all cases the $4f$ - 1 configuration is stabilized relative to the $4f$ with decreasing volume. The small-gap semiconductor CeNiSn does not follow the expected response to pressure; instead of $\partial\Delta/\partial P$ being positive, the gap closes at a rate $\partial\Delta/\partial P \approx -0.03$ kbar $^{-1}$ and extrapolates to $\Delta=0$ at a critical pressure of about 30 kbar.³⁰ A possible interpretation is that the anisotropic gap³¹, not observed in these measurements on a polycrystalline sample³⁰, is shunted by conduction through non-gapped regions of the Fermi surface. Pressure studies on single crystals of CeNiSn should prove valuable in resolving this possibility.

Substitution Studies

Lutetium substitutions³² for Yb in YbB_{12} and La substitutions³³ for Sm in SmB_6 rapidly metallize these Kondo insulators which have gaps comparable^{2,4,6} to $\text{Ce}_3\text{Bi}_4\text{Pt}_3$. Because Lu is smaller than Yb but La is larger than Sm, this immediately suggests that the primary role of the dopant is not to suppress the gap by chemical pressure. However, in both cases the $4f$ -sublattice periodicity is broken and nonmagnetic, trivalent atoms replace those with some divalent character.

In the case of $(\text{Ce}_{1-x}\text{La}_x)_3\text{Bi}_4\text{Pt}_3$, La substitutions also induce a metallic, Kondo-like state, shift the maximum in χ to lower temperatures and produce a contribution to the electronic specific heat γ that is consistent with a Kondo temperature of about 300K.⁶ Previously we have established¹² that, for La concentrations above about $x=0.20$, $\gamma \propto 1/T\chi$. Experimentally, the proportionality agrees quantitatively with the prediction from a Bethe ansatz solution of the Coqblin-Schrieffer model. Figure 7 shows that within uncertainties in absolute values of x the electronic specific heat per mole Ce is also proportional to \sqrt{x} over the range studied $0.015 \leq x \leq 0.5$. Such a relationship has been predicted³⁴ recently to arise from an impurity band of Kondo holes produced by breaking translational invariance of the Ce sublattice through non-magnetic substitutions. (We note that in $\text{Ce}_3\text{Bi}_4(\text{Pt}_1-x\text{Au}_x)_3$, gold substitutions for Pt also metallize the compound but in this case $\gamma \propto x$ for $x=0.1$ and 0.2 .)

Similar studies have not been performed for other rare-earth (RE) substitutions. However, resistivity, susceptibility and specific heat have been measured¹³ on a series of $(\text{Ce}_{0.985}\text{RE}_{0.015})_3\text{Bi}_4\text{Pt}_3$ crystals. Detailed analysis of the specific heat is complicated by a low-temperature upturn in C/T that scales approximately with the spin of the rare-earth

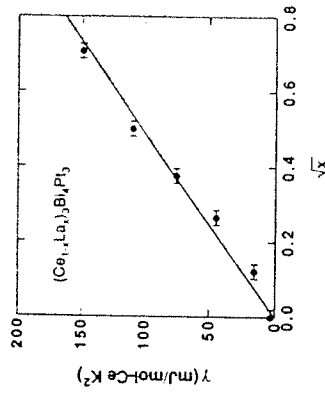


Fig. 7. Linear contribution to the specific heat $\gamma \approx C/T$ at low temperature for $(\text{Ce}_{1-x}\text{La}_x)_3\text{Bi}_4\text{Pt}_3$ versus the square root of La concentration x .

dopant. However, a linear extrapolation of C/T vs T^2 from above the upturn to $T=0$ gives $C/T|_{T=0} = 16 \pm 6$ mJ/mole-Ce-K² for all seven rare-earth dopants. This result argues again that chemical pressure is not a dominant effect and that the increase in C/T for small x is independent of the magnetic character of the substituted element as expected³⁶ in a Kondo-hole interpretation, provided the low-temperature tail in C/T is not intrinsic to the correlated-electron ground state. This last point has not been resolved and deserves further attention, particularly in light of resistivity and susceptibility measurements that exhibit non-monotonic trends with RE substituents. Most pronounced is the resistivity that tends toward metallization for rare-earths lighter than Ho and toward more strongly semiconducting behavior for heavier rare earths.

Although arguments have been made that chemical pressure is not a dominant effect in substituted alloys, pressure does play a role. Shown in Fig. 8 is the resistance of $(\text{Ce}_{0.985}\text{La}_{0.015})_3\text{Bi}_4\text{Pt}_3$ at applied pressures to 18 kbar. The temperature-dependent resistance at ambient pressure is typical of $(\text{Ce}_{0.985}\text{RE}_{0.015})_3\text{Bi}_4\text{Pt}_3$ compounds for rare-earths lighter than Ho and of mixed-valent metals, eg. CePd_3 , in which the Ce sublattice periodicity has been broken by non-magnetic or magnetic substitutions.³⁶ With increasing pressure (increasing hybridization) there is a clear trend for the resistance to approach that of the undoped compound. A linear extrapolation between the lattice parameters of $\text{La}_3\text{Bi}_4\text{Pt}_3$ and $\text{Ce}_3\text{Bi}_4\text{Pt}_3$, combined with a bulk modulus of 950 kbar, allows an estimate of ~ 3 kbar for the negative chemical pressure induced by substituting the larger La atom for Ce. Although local chemical pressure around the dopant must be larger than this estimate, the data of Fig. 8 suggest an applied pressure of 30 to 40 kbar would be required to reproduce $\rho(T)$ of undoped $\text{Ce}_3\text{Bi}_4\text{Pt}_3$. Comparison of data for $P=12.4$ and 18.0 kbar shows a qualitative change in the low-temperature dependence of $\rho(T)$ that could be associated with a metal-insulator transition in the Kondo-hole band that is formed by La substitutions. Higher pressure experiments on this material and on more heavily doped compounds would be helpful in clarifying this possibility.

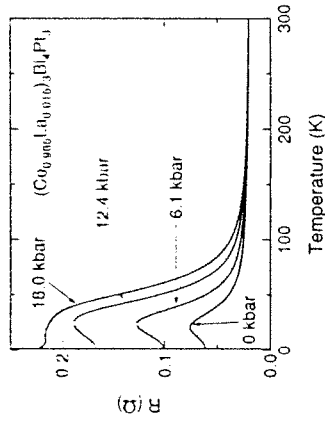


Fig. 8. Resistance as a function of temperature for $(\text{Ce}_{0.985}\text{La}_{0.015})\text{Bi}_4\text{Pt}_3$ under various applied hydrostatic pressures.

Attempts to replace Ce with tetravalent ions, such as Zr and Th, have been unsuccessful in $\text{Ce}_3\text{Bi}_4\text{Pt}_3$. However, a pronounced asymmetry has been observed³⁷ in trivalent doping in the Kondo insulators, orthorhombic CeRhSb and cubic $\text{U}_3\text{Sb}_4\text{Pt}_3$. Substituting 10% La in CeRhSb destroys the small, $\sim 7\text{K}$, gap; whereas, the same amount of Zr makes the sample more resistive at all temperatures below 300K. Three percent Y or Lu in $\text{U}_3\text{Sb}_4\text{Pt}_3$ decreases the low-temperature resistivity and enhances the electronic specific heat by about one order of magnitude. On the other hand up to 10% Th addition causes no change in γ .

DISCUSSION

The body of data presented for $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ and existing in the literature for related small-gap semiconductors is consistent with their being Kondo-like metals at temperatures $T \geq E_g/k_B$. Purely trivalent, isostructural analogues are normal metals at all temperatures; whereas, isostructural compounds formed with an element having the anomalous valence of the rare-earth it replaces, e.g., tetravalent elements replacing Ce or divalent elements replacing Sm or Yb, often are conventional semiconductors.^{13,21} An example is EuB_6 , in which Eu is divalent and which has a large gap, but SmB_6 , in which Sm is nearly trivalent, has a small semiconducting gap. The existence of these isostructural conventional semiconductors indicates that the band structure near the Fermi level in Kondo insulators is relatively simple. We believe this is why most Kondo insulators form in cubic crystal structures, i.e., very loosely, simple crystal and band structures are mutually compatible.

The modestly large electronic specific heat that develops when the Kondo insulator is metallized by doping^{12,38} or by pressure³, quasi-elastic neutron scattering at high

temperatures that evolves into a well-defined gap in the spin-spin correlation function at low temperature¹⁵, and the inter-relationship between $4f$ -derived thermal expansion, static susceptibility and the spin gap are incontrovertible evidence that the charge-excitation gap originates from spin/change hybridization between the $4f$ electron and the underlying s.p. band structure. In mixed-valent metals this behavior is believed to be described by the Anderson Lattice Hamiltonian. In this model many-body interactions renormalize the band f level to be degenerate with the conduction band, allowing hybridization between conduction electrons and the renormalized f level. Generally there will be more than one conduction band crossing the Fermi level and in this case it is easy to argue that the resulting hybridized-band structure will produce a metallic ground state.²¹ However, there is only a single conduction band cutting E_F and the electron count, which includes the strongly interacting f -electrons, is exactly two, the lower-hybridized band will be filled and the upper band empty. Under these conditions, a mean-field treatment of the Anderson Lattice Hamiltonian predicts^{39,40} an indirect gap for excitations from the zone center to zone boundary proportional to $(1-n_f)V^2D$, where n_f is the f occupation, V is the hybridization matrix element and D is the conduction-band density of states. This interpretation** has a number of interesting consequences: at temperatures greater than E_g/k_B , the physics of Kondo insulators and metals is identical; the low-temperature transport and magnetic gaps have a common origin and should be of comparable magnitude, as experimentally observed; the existence of isostructural compounds having conventional semiconducting gap, i.e., not induced by electronic correlations, provide experimental proof that the Fermi-surface volume, in these cases zero, is independent of the Coulomb repulsion U , as expected from Luttinger's theorem^{21,39}; an asymmetry in the thermodynamics is expected³⁹ between electron and hole doping, as observed, because Coulomb interactions forbid doping by more than one electron per f ion but there is no such restriction for hole doping; and the temperature dependence of the static susceptibility below T_X arises from intraband processes allowed by thermal population of holes at finite T , i.e., interactions, characterized by a Curie-Weiss Θ_p are not required to explain $\chi(T)$ at low T .

CONCLUSIONS

Kondo insulators appear to be an unusually simple realization of the Anderson Lattice Hamiltonian in which the lower-hybridization band is exactly filled, or in Kondo language the Abrikosov-Suhl resonance exactly fills a Brillouin zone. As such, this class of materials offers the possibility of detailed comparison between theory and experiment in the hope of a more complete understanding of both strongly-correlated insulators and metals.

Acknowledgments

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Footnotes

- * Because the temperature range over which the activation energy is evaluated is larger than or comparable to Δ , Δ and E_g may be underestimated by ~20%.
- + We thank G. Aeppli for this suggestion.
- ** Strictly, the model is for a doubly degenerate ground state. Inelastic neutron scattering (Ref. 15) finds no evidence for crystal-field splitting of the $J=5/2$ manifold in $\text{Ce}_3\text{Bi}_4\text{Pt}_3$. In spite of this, the calculation should reflect qualitatively the essential physics at larger degeneracy.

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ORIGIN OF GAP FORMATION IN $\text{Ce}_3\text{Pt}_3\text{Sb}_4$ AND $\text{Ce}_3\text{Pt}_3\text{Bi}_4$

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INTRODUCTION

Valence fluctuation systems with an energy gap of activation type have been attracting much attention to investigate the origin of gap formation. SmB_6 , SmS , and YbP_{12} are well known to have clear gap.^{1,2} The existence of gap has been experimentally suggested in CeNiSn , $\text{Ce}(\text{Pd}_{1-x}\text{Cu}_x)_3$, CeRhSb , and TmSe .^{1,2,3}

Recently, new groups of ternary compounds containing Ce or U have been found to show semiconductor-like behavior.^{2,3,4,5} The first group is UNiSn , UPtSn and URhSn the second $\text{U}_3\text{T}_3\text{Sb}_4$ ($\text{T} = \text{Ni}, \text{Pd}, \text{Pt}$) and $\text{Ce}_3\text{Au}_3\text{Sb}_4$, and the third $\text{Ce}_3\text{Pt}_3\text{X}_4$ ($\text{X} = \text{Sb}, \text{Bi}$)^{3,4,5} that is the subject of this report. All of these ternary compounds have a characteristic crystal structure; a transition or a noble metal atom is placed at the largest empty site of corresponding binary compound.² In the first and second groups, as electrons are well localized and have a large magnetic moment, an origin of gap formation has been explained from band structures of non-*f* reference Th- or La-compounds. Furthermore the band structures of the ternary compounds are understood on the basis of those of the corresponding binary compounds because of the characteristic crystal structure. The third group compounds belong to the valence fluctuation regime because the magnetic susceptibility of these compounds is typical for a valence fluctuating compound.^{3,4,5} Thus the ground state is considered to be different from the first and second groups.

In recent years, there is notable progress in the Fermi surface study for Ce compounds.^{6,7} For the materials belonging to the valence fluctuation regime, the Fermi surfaces can be explained very well by conventional band calculations. This implies that the *f*-electrons are itinerant in the ground state and contribute directly to the formation of the Fermi surface. However, cyclotron effective masses cannot be explained

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