

Los Alamos National Laboratory is operated by the University of California for the United States Department of Energy under contract W-7405-ENG-36

TITLE THERMODYNAMICS AND TRANSPORT IN CERIUM<sub>3</sub>BISMUTH<sub>4</sub>PLATINUM<sub>3</sub>  
AND RELATED COMPOUNDS

AUTHOR(S) J.D. Thompson, W.P. Beyermann, P.C. Canfield, M.F. Hundley,  
G.H. Kwei, A. Lacerda, Z. Fisk, R.S. Kwok, J.M. Lawrence and  
A. Severing

SUBMITTED TO Invited paper for TRANSPORT AND THERMAL PROPERTIES OF  
f ELECTRON SYSTEMS  
ed. H. Fujii, T. Fujita and G. Oomi, Plenum Publishing

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Received by OSTI  
11/9/92

By acceptance of this article, the publisher recognizes that the U.S. Government retains a nonexclusive, royalty free license to publish or reproduce the published form of this contribution, or to allow others to do so for U.S. Government purposes.

The Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy.

Los Alamos **MASTER** Los Alamos National Laboratory  
Los Alamos, New Mexico 87545

SR

THERMODYNAMICS AND TRANSPORT IN  $\text{Ce}_3\text{Bi}_4\text{Pt}_3$  AND RELATED COMPOUNDS

J. D. Thompson, P-10  
W. P. Beyermann, P-10  
P. C. Canfield, P-10  
M. F. Hundley, P-10  
G. H. Kwei, P-10  
A. Lacerda, P-10  
Z. Fisk, CMS  
R. S. Kwok, Hughes Aircraft  
J. M. Lawrence, U. C. Irvine  
A. Severing, Institut Laue-Langevin

Invited Paper for TRANSPORT AND THERMAL PROPERTIES OF f ELECTRON SYSTEMS  
Submitted August 19, 1992  
LA-UR-92-

Our discovery of semiconducting behavior in the mixed-valence compound  $\text{Ce}_3\text{Bi}_4\text{Pt}_3$  has revitalized theoretical and experimental interest in related systems, eg.  $\text{SmB}_6$ ,  $\text{YbB}_{12}$ , and  $\text{SmS}$ , which have been known for over a decade. Before  $\text{Ce}_3\text{Bi}_4\text{Pt}_3$  these other compounds were considered curiosities among mixed-valent materials, which normally are metallic-like. With the addition of  $\text{Ce}_3\text{Bi}_4\text{Pt}_3$  and recently others, such as  $\text{CeNiSn}$ ,  $\text{CeRhSb}$  and  $\text{U}_3\text{Sb}_4\text{Pt}_3$ , it has become clear that these semiconductors, with energy gaps typically 10 - 100 K, form an important subset of materials with strong electronic correlations, now called Kondo insulators. We have characterized single crystals of  $\text{Ce}_3\text{Bi}_4\text{Pt}_3$  through temperature dependent resistivity and lattice constant at ambient and high pressures, Hall number, magnetoresistance, thermoelectric power, magnetic susceptibility, specific heat and inelastic neutron scattering measurements, as well as through various substitutions for Ce and Pt. Results of these measurements are reviewed and compared to what is known about other mixed-valent metals and insulators. Although much remains to be explored, it appears that Kondo insulators can be described as an unusually simple realization of the Anderson Lattice Hamiltonian. In this Hamiltonian, strong electronic correlations renormalized the bare f-level to be degenerate with the conduction band such that the

renormalized f-level hybridizes with conduction electrons to form lower and upper hybridized bands. A semiconducting ground state may appear if the renormalized f-level hybridizes with only a single, broad conduction band at the Fermi energy. If 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. As such, this class of materials offers the possibility of a detailed comparison between theory and experiment and the hope of a more complete understanding of both strongly correlated insulators and metals.

## **THERMODYNAMICS AND TRANSPORT IN $Ce_3Bi_4Pt_3$ AND RELATED MATERIALS**

J.D. Thompson<sup>1</sup>, W.P. Beyermann<sup>1,2</sup>, P.C. Canfield<sup>1</sup>, Z. Fisk<sup>1</sup>, M.F. Hundley<sup>1</sup>, G.H. Kwei<sup>1</sup>, R.S. Kwok<sup>1,3</sup>, A. Lacerda<sup>1</sup>, J.M. Lawrence<sup>4</sup>, and A. Severing<sup>5</sup>

<sup>1</sup>Los Alamos National Laboratory, Los Alamos, NM  
87545

<sup>2</sup>Department of Physics, University of California,  
Riverside, CA 92521

<sup>3</sup>Hughes Aircraft, Los Angeles, CA 90009

<sup>4</sup>Department of Physics, University of California,  
Irvine, CA 92717

<sup>5</sup>Institut Laue-Langevin, 38042 Grenoble, FRANCE

### **INTRODUCTION**

The interplay between electronic and magnetic correlations in certain 4f and 5f intermetallic compounds has been shown<sup>1</sup> 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<sub>6</sub> (Ref. 2), SmS (Ref. 3), and YbB<sub>12</sub> (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<sup>5-8</sup> and U<sup>9</sup> 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<sup>10,11</sup>. In the following we review transport and thermodynamic properties of the small-gap semiconductor  $\text{Ce}_3\text{Bi}_4\text{Pt}_3$  and discuss them in relation to what is known about other Kondo insulators and metals.

## RESULTS

### $\text{Ce}_3\text{Bi}_4\text{Pt}_3$

Figure 1 compares the temperature-dependent resistivity  $\rho(T)$  of single crystal  $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ ,  $\text{La}_3\text{Bi}_4\text{Pt}_3$  and  $\text{Pr}_3\text{Bi}_4\text{Pt}_3$ . 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  $\text{Ce}_3\text{Bi}_4\text{Pt}_3$  data shows activated behavior above approximately 50K, with an activation energy  $\Delta=50\text{K}$  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  $\Delta$  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  $\rho(2\text{K})/\rho(300\text{K})$  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  $R_H$  and thermoelectric power measurements<sup>12</sup> which show above about 50K temperature dependences characteristic of an electronic gap  $E_g=100\text{K}$ , 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<sup>13</sup>,  $\mu=R_H/\rho$ , saturates to a small, temperature-independent value of  $10 \text{ cm}^2/\text{V}\cdot\text{sec}$ , suggesting strong scattering of carriers with enhanced effective mass.

As to be expected for a small-gap semiconductor, the electronic contribution to the specific heat<sup>6</sup> of  $\text{Ce}_3\text{Bi}_4\text{Pt}_3$  is small,  $\gamma = 3\text{mJ}/\text{mole}\cdot\text{Ce}\cdot\text{K}^2$ , a value about one-third that of

$\text{La}_3\text{Bi}_4\text{Pt}_3$ . 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  $1.5 < T < 20\text{K}$  of the measurements. This result contrasts to observations<sup>14</sup> on the orthorhombic, small-gap ( $\Delta = 5\text{K}$ ) semiconductor  $\text{CeNi}$  which  $\text{Sn}$  in  $C/T$  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  $\text{CeNiSn}$ . 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  $\chi$  and thermal expansion of  $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ . Figure 2 shows  $\chi$  versus temperature for a  $\text{Ce}_3\text{Bi}_4\text{Pt}_3$  crystal produced from Ames Laboratory Ce. The temperature dependence is Curie-Weiss above  $\sim 100\text{K}$ , with an effective moment  $\mu_{\text{eff}} = 2.42\mu_{\text{B}}/\text{Ce}$  and a paramagnetic  $\Theta_{\text{p}} = -125\text{K}$ . The broad peak in  $\chi$ , centered at  $T_{\chi} = 80\text{K}$ , is characteristic of metallic mixed-valence compounds having a Kondo temperature  $T_{\text{K}} \approx (3-4)T_{\chi} = 240-320\text{K}$  (Ref. 6). In contrast to earlier measurements<sup>6</sup> 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/mole-Ce. 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  $\Delta$ .

Inelastic neutron scattering measurements<sup>15</sup> on powdered single crystals reproduce the temperature dependence of the static susceptibility, as also shown in Fig. 2. What is 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  $E_{\text{g}}$  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  $T_{\text{K}}$  inferred from susceptibility measurements. Similar conclusions are drawn from NMR studies<sup>16</sup>. Evidence for a spin-gap has also been reported in the small-gap semiconductor  $\text{CeNiSn}$ <sup>17</sup> and in the mixed-valent metal  $\text{YbAl}_3$  (Ref. 18).

Temperature variations in the cubic lattice parameters  $a_0$  of  $\text{Ce}_3\text{Bi}_4\text{Pt}_3$  and  $\text{La}_3\text{Bi}_4\text{Pt}_3$  are given in Fig. 3(a). An anomalous decrease in  $a_0$  is seen below 100K for  $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ , which for metallic Ce compounds would be argued as an indication of admixed  $4f^0$  and  $4f^1$  configurations. (Preliminary  $L_{\text{III}}$ -edge x-ray absorption experiments on  $\text{Ce}_3\text{Bi}_4\text{Pt}_3$

indicate an f-occupancy  $n_f \approx 0.9$ )<sup>19</sup>. The 4f-contribution to the volume-thermal expansion is displayed more obviously in Fig. 3(b) where the volume thermal expansion coefficient  $\beta = 3\partial(\ln a_0)/\partial T$  of both compounds and their difference  $\Delta\beta = \beta_{Ce} - \beta_{La}$  are plotted as a function of temperature. The difference  $\Delta\beta$  peaks at  $T\Delta\beta \approx 50K$ . By Maxwell's relations, then, the pressure derivative of the 4f entropy also peaks at  $T\Delta\beta$ . Similar measurements<sup>20</sup> performed with the samples subjected to an applied pressure of 17.7 kbar give  $T\Delta\beta \approx 85K$  and, from a comparison of the ambient and high pressure data for  $Ce_3Bi_4Pt_3$ , a  $T \rightarrow 0$  bulk modulus of about 950 kbar. An analysis of these results yields a Gruneisen parameter  $\Omega=36$  comparable to that expected of a metallic-mixed valent compound with a  $T_K$  of 200-300K.

A remarkable observation<sup>13</sup> is that the difference in lattice parameters  $\Delta a_0$  between that of  $Ce_3Bi_4Pt_3$  and  $La_3Bi_4Pt_3$  is linear in the product  $\chi T$ , as shown in Fig. 4(a). In the absence of interactions,  $\chi T$  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<sup>+</sup> 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 magnitude to the value of the gap in the spin-spin correlation function measured at low temperatures by inelastic neutron scattering<sup>15</sup> and to the paramagnetic  $\Theta_p$  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  $\chi$  above  $\sim 30K$  confirms consistency in the parameterizations of  $\Delta a_0(T)$ ; but perhaps more significant is that when  $\chi(T)$  is viewed this way no Curie-Weiss  $\Theta_p$ , ie., no interactions in the conventional sense, is required to understand the temperature variations in  $\chi$  at low  $T$ <sup>21</sup>.

To probe the ground state of  $Ce_3Bi_4Pt_3$  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  $Ce_3Bi_4Pt_3$  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 measurements<sup>22</sup> 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  $\Delta$ . Similar results have been reported<sup>23</sup> for  $CeNiSn$  with  $H=11T$  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  $\omega_c\tau = 1$  at about 1T, where  $\omega_c$  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.

From the linear relationship found in Fig. 4(b) and the observation<sup>20</sup> that at low temperatures  $\Delta a_0$  increases with pressure, it is straightforward to show that  $\partial\Delta/\partial P > 0$ , if  $\Delta$  in Fig. 4(b) is associated with the spin or charge gap. That is, decreasing the cell volume, which favors stronger admixture of the  $4f^0$  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  $\partial\ln\Delta/\partial P$  ranges from 0.05 to 0.16  $\text{kbar}^{-1}$  consistent with the Grüneisen interpretation of the pressure-dependent thermal expansion.<sup>29</sup> This result contrasts to observations<sup>25,26</sup> on  $\text{SmB}_6$  and  $\text{YbB}_{12}$  in which pressure suppresses the electronic gap. In the case of  $\text{SmB}_6$ ,  $\partial\ln\Delta/\partial P$  varies from -0.02 to about -0.03  $\text{kbar}^{-1}$  depending on the sample. (The sign difference between  $\text{Ce}_3\text{Bi}_4\text{Pt}_3$  and  $\text{SmB}_6$  in their logarithmic derivatives of  $\Delta$  are reflected as well in sign differences in their 4f-derived thermal expansion<sup>20,27</sup>.)

At pressures of 55 to 70 kbar the electronic gap in  $\text{SmB}_6$  is closed and the temperature-dependent resistance becomes that of a typical Kondo-lattice metal<sup>10,25</sup>. X-ray diffraction at room temperature indicates<sup>28</sup> 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  $4f^6$  ( $J=0$ ), leading to a decrease in charge hybridization and an approach to the Kondo-limit. Similar arguments apply to  $\text{YbB}_{12}$ . 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,  $\Delta$  tracks the expected change<sup>29</sup> with pressure in charge/spin hybridization and not band filling because in all cases the  $4f^{n-1}$  configuration is stabilized relative to the  $4f^n$  with decreasing volume. The small-gap semiconductor  $\text{CeNiSn}$  does not follow the expected response to pressure;

instead of  $\partial\Delta/\partial P$  being positive, the gap closes at a rate  $\partial\ell^{\text{r}}\Delta/\partial P = -0.03 \text{ kbar}^{-1}$  and extrapolates to  $\Delta=0$  at a critical pressure of about 30 kbar<sup>30</sup>. A possible interpretation is that the anisotropic gap<sup>31</sup>, not observed in these measurements on a polycrystalline sample<sup>30</sup>, 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 substitutions<sup>32</sup> for Yb in YbB<sub>12</sub> and La substitutions<sup>33</sup> for Sm in SmB<sub>6</sub> rapidly metallize these Kondo insulators which have gaps comparable<sup>2,4,6</sup> to Ce<sub>3</sub>Bi<sub>4</sub>Pt<sub>3</sub>. 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 (Ce<sub>1-x</sub>La<sub>x</sub>)<sub>3</sub>Bi<sub>4</sub>Pt<sub>3</sub>, La substitutions also induce a metallic, Kondo-like state, shift the maximum in  $\chi$  to lower temperatures and produce a contribution to the electronic specific heat  $\gamma$  that is consistent with a Kondo temperature of about 300K<sup>6</sup>. Previously we have established<sup>12</sup> 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 predicted<sup>34</sup> 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 Ce<sub>3</sub>Bi<sub>4</sub>(Pt<sub>1-x</sub>Au<sub>x</sub>)<sub>3</sub>, 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 measured<sup>35</sup> on a series of (Ce<sub>0.985</sub>RE<sub>0.015</sub>)<sub>3</sub>Bi<sub>4</sub>Pt<sub>3</sub> 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 dopant. However, a linear extrapolation of  $C/T$  vs  $T^2$  from above the upturn to  $T=0$  gives  $C/T|_{T=0} = 50 \pm 20 \text{ mJ/mole}\cdot\text{Ce}\cdot\text{K}^2$  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 expected<sup>36</sup> 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 re-

solved 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 Figure 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.  $\text{CePd}_3$ , in which the Ce sublattice periodicity has been broken by non-magnetic or magnetic substitutions<sup>36</sup>. 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.

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 observed<sup>37</sup> in tri-versus tetravalent doping in the Kondo insulators, orthorhombic  $\text{CeRbSb}$  and cubic  $\text{U}_3\text{Sb}_4\text{Pt}_3$ . Substituting 10% La in  $\text{CeRbSb}$  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  $\gamma$ .

## 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<sup>13,21</sup>. An example is  $\text{EuB}_6$ , in which Eu is divalent and which has a large gap, but  $\text{SmB}_6$ , 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<sup>12,38</sup> or by pressure<sup>3</sup>, quasi-elastic neutron scattering at high temperatures that evolves into a well-defined gap in the spin-spin correlation function at low temperature<sup>15</sup>, 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,d 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 bare 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<sup>21</sup>. However, if 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<sup>39,40</sup> 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 a conventional semiconducting gap, i.e., not induced by electronic correlations, provides experimental proof that the Fermi-surface volume, in these cases zero, is independent of the Coulomb repulsion U, as expected from Luttinger's theorem<sup>21,39</sup>; an asymmetry in the thermodynamics is expected<sup>39</sup> 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  $\Theta_p$  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 and the hope of a more complete understanding of both strongly-correlated insulators and metals.

### **Acknowledgments**

We thank G. Aeppli, P.S. Riseborough and P. Schlottmann for helpful discussions. Work at Los Alamos was performed under the auspices of the U.S. Department of Energy.

## FIGURE CAPTIONS

Fig. 1. Resistivity, plotted on a logarithmic scale, as a function of temperature for single crystals of  $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ ,  $\text{La}_3\text{Bi}_4\text{Pt}_3$  and  $\text{Pr}_3\text{Bi}_4\text{Pt}_3$ . Above approximately 350K, the resistivity of  $\text{Ce}_3\text{Bi}_4\text{Pt}_3$  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  $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ .

Fig. 2. Magnetic susceptibility  $\chi$  versus temperature for  $\text{Ce}_3\text{Bi}_4\text{Pt}_3$  measured in a field of 1T. Open circles denote  $\chi$  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  $T=2\text{K}$  for an incident neutron energy of 69 meV. A gap in the spin-spin correlation function of 12meV is apparent.

Fig. 3. (a) Cubic lattice parameter, determined by Rietveld analysis of neutron-diffraction spectra, of  $\text{Ce}_3\text{Bi}_4\text{Pt}_3$  and  $\text{La}_3\text{Bi}_4\text{Pt}_3$  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.

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)  $\Delta a_0$  versus  $1/[1 + \exp(\Delta/k_B T)]$ . A linear relationship is found for  $\Delta/k_B = 120 \pm 5\text{K}$ .

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.

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

Fig. 7. Linear contribution to the specific heat  $\gamma = C/T$  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  $x$ .

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

## Footnotes

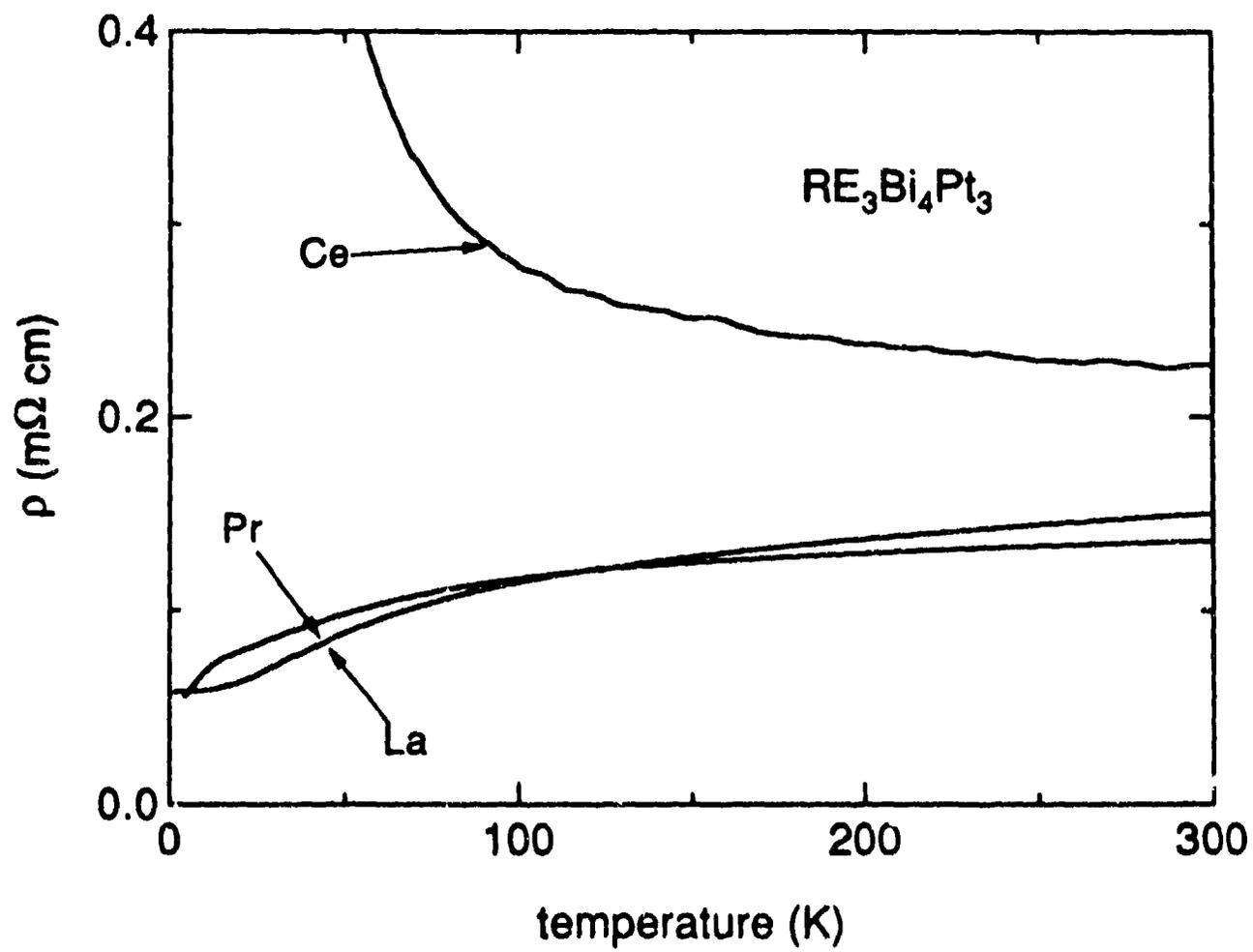
- \* Because the temperature range over which the activation energy is evaluated is larger than or comparable to  $D$ ,  $D$  and  $E_g$  may be underestimated by  $\sim 20\%$ .
- + We thank G. Aepli for this suggestion.
- \*\* Strictly, the model is for a doubly degenerate ground state. Inelastic neutron 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.

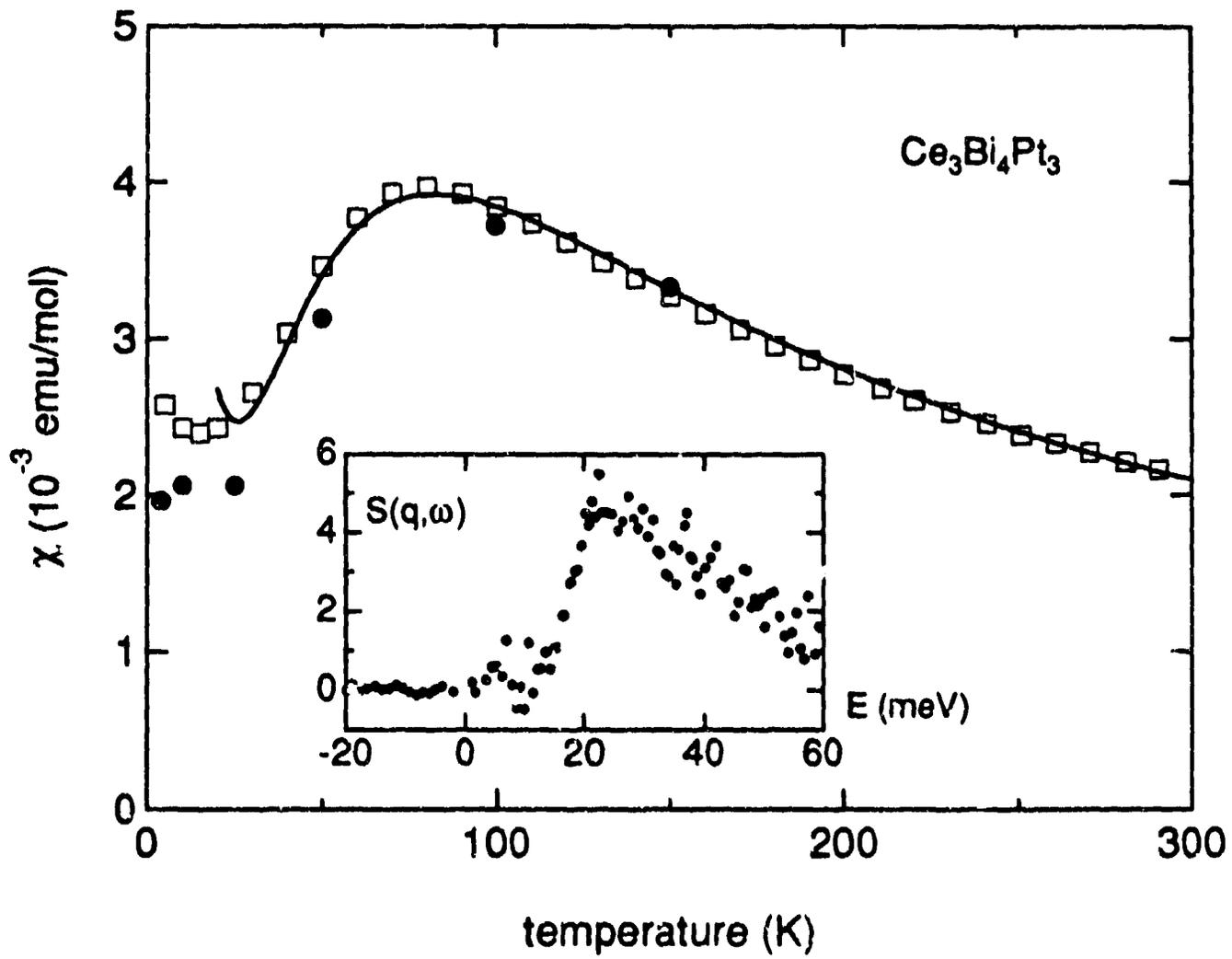
## REFERENCES

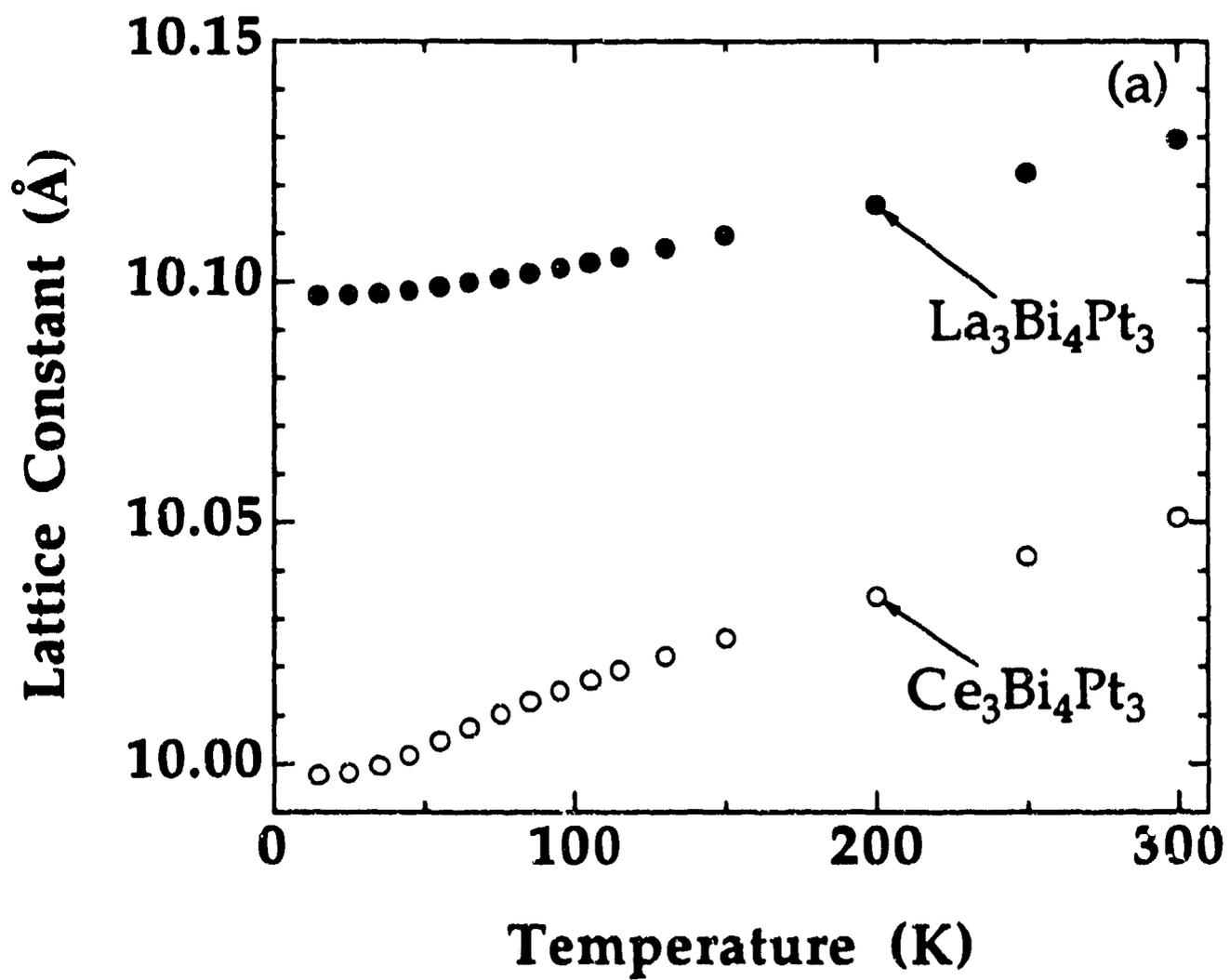
1. See, for example, N. Grewe and F. Steglich, Heavy Fermions, in: "Handbook on the Physics and Chemistry of Rare Earths", Vol. 14, K. A. Gschneidner and L. Eyring, ed. Elsevier Science Publishers, Amsterdam (1991).
2. S. von Molnar et al., Study of the energy gap in single crystal  $\text{SmB}_6$ , in: "Valence Instabilities," P. Wachter and H. Boppart, ed. North-Holland, Amsterdam (1982); A. Menth, E. Buehler and T. H. Geballe, Magnetic and semiconducting properties of  $\text{SmB}_6$ , Phys. Rev. Lett. 22: 295 (1969).
3. D. Bader, N. E. Phillips and D. B. McWhan, Heat capacity and resistivity of metallic  $\text{SmS}$  at high pressure, Phys. Rev. B 7: 4686 (1973).
4. M. Kazaya et al., Mixed valence properties of  $\text{YbB}_{12}$ , J. Magn. Magn. Mat. 47 & 48: 429 (1985).
5. T. Takabatake, Y. Nakazawa and M. Ishikawa, Gap formation in the valence fluctuation system  $\text{CeNiSn}$ , Jpn. J. Appl. Phys. 26, Suppl. 26-3: 547 (1987); F. G. Aliev et al., Transport and magnetic properties of intermetallic systems  $\text{RNiM}$  ( $R=\text{U, Ce, Er, Ho, Tm, Yb, Sc, Ti, Zr, Hf}$ ;  $M=\text{Sn, Sb}$ ), J. Magn. Magn. Mat. 76 & 77: 295 (1988).
6. M. F. Hundley et al., Hybridization gap in  $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ , Phys. Rev. B 42: 6842 (1990).
7. K. Malik and D. T. Adroja, Evidence of pseudogap formation in a new valence-fluctuating compound:  $\text{CeRhSb}$ , Phys. Rev. B 43: 6267 (1991).
8. M. Kazaya, K. Katoh and K. Takegaraha, Semiconducting properties of the isomorphous compounds  $\text{Ce}_3\text{Au}_3\text{Sb}_4$  and  $\text{Ce}_3\text{Pt}_3\text{Sb}_4$ , Solid State Commun. 78: 797 (1991).
9. T. Takabatake et al., Heavy-fermion and semiconducting properties of the ternary uranium compounds  $\text{U}_3\text{T}_3\text{Sn}_4$  and  $\text{U}_3\text{T}_3\text{Sb}_4$  ( $T=\text{Ni, Cu, Pd, Pt}$  and  $\text{Au}$ ), J. Phys. Soc. Jpn. 59: 4412 (1990).
10. V. Moshchalkov et al.,  $\text{SmB}_6$  at high pressures: the transition from insulating to the metallic Kondo lattice, J. Magn. Magn. Mat. 47 & 48: 289 (1985).
11. A. J. Millis, Heavy electron metals and insulators, in: Physical Phenomena at High magnetic Fields, E. Manousakis, P. Schlottmann, P. Kumar, K. Bedell and F. M. Mueller, ed., Addison-Wesley, Redwood (1991).
12. M. F. Hundley et al., Evidence for a coherence gap in  $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ , Physica B 171: 254 (1991).
13. Z. Fisk et al.,  $\text{Ce}_3\text{Bi}_4\text{Pt}_3$  and hybridization gap physics, J. Alloys Compds. 181: 369 (1992).

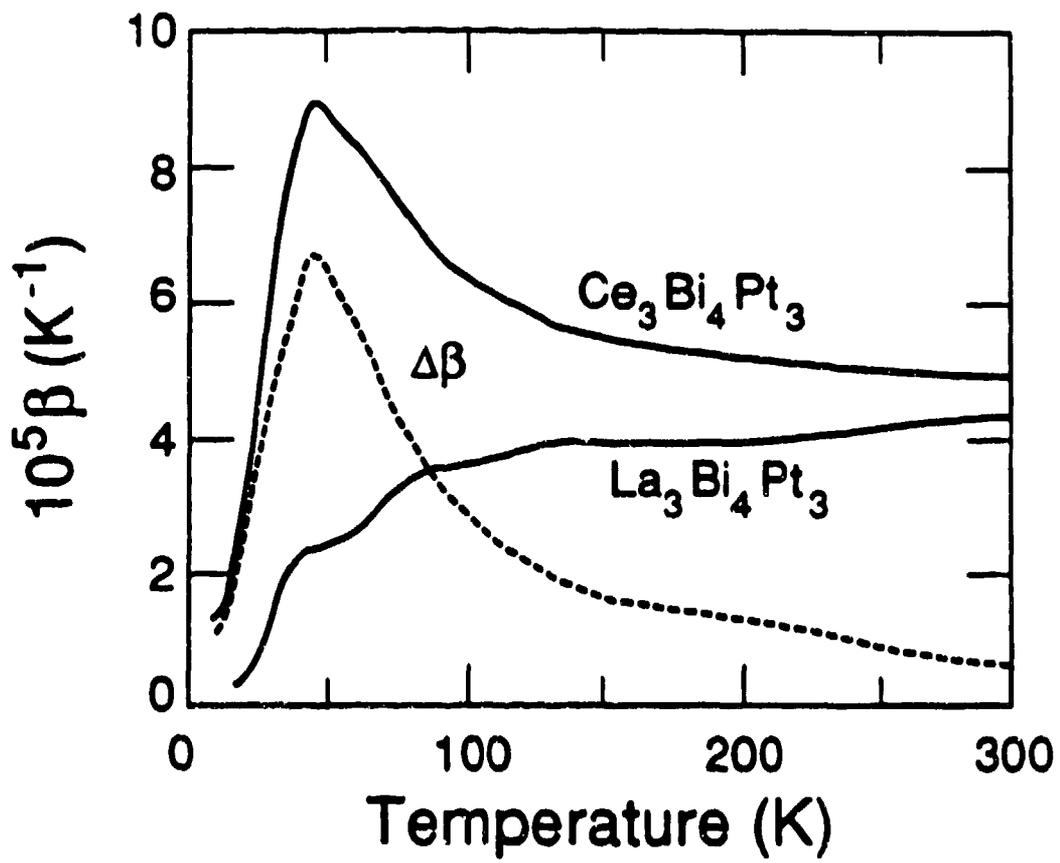
14. T. Takahatake et al., Anisotropic suppression of the energy gap in CeNiSn by high magnetic fields, *Phys. Rev. B* 45: 5740 (1992-II).
15. A. Severing et al., Gap in the magnetic excitation spectrum of Ce<sub>3</sub>Bi<sub>4</sub>Pt<sub>3</sub>, *Phys. Rev. B* 44: 6832 (1991-I).
16. A. P. Reyes et al., (unpublished).
17. T. E. Mason et al., Spin gap and antiferromagnetic correlations in the Kondo insulator CeNiSn, *Phys. Rev. Lett.* 69: 490 (1992).
18. A. P. Murani, Observation of f-band hybridization gap in the anomalous rare-earth compound YbAl<sub>3</sub>, *Phys. Rev. Lett.* 54: 1444 (1985).
19. G. H. Kwei et al., (unpublished).
20. G. H. Kwei et al., Thermal expansion of Ce<sub>3</sub>Bi<sub>4</sub>Pt<sub>3</sub> at ambient and high pressures, *Phys. Rev. B* (in press).
21. G. Aeppli and Z. Fisk, Kondo insulators, *Comm. Cond. Mat. Phys.* (in press).
22. G. Boebinger et al., (unpublished).
23. T. Takahatake et al., Magnetoresistance and Hall effect in the Kondo-lattice system CeNiSn with an anisotropic energy gap, *J. Magn. Magn. Mat.* 108: 155 (1992).
24. M. F. Hundley et al., Magnetoresistance of the Kondo insulator Ce<sub>3</sub>Bi<sub>4</sub>Pt<sub>3</sub>, *Physica B* (in press).
25. J. Beille et al., Suppression of the energy gap in SmB<sub>6</sub> under pressure, *Phys. Rev. B* 28: 7397 (1983).
26. F. Iga, "Experimental Study of Intermediate Valence Compound YbB<sub>12</sub>", Ph.D. thesis, Tohoku University (1988).
27. T. Kasuya et al., Anomalous properties of valence fluctuating CeB<sub>6</sub> and SmB<sub>6</sub> in: "Valence Fluctuations in Solids", L. M. Falicov, W. Hanke and M. B. Maple, ed., North-Holland, Amsterdam (1981).
28. H. E. King et al., Effects of valence and intermediate valence on the compressibility of the rare-earth hexaborides, in: "Valence Fluctuations in Solids," L. M. Falicov, W. Hanke and M. B. Maple, ed., North-Holland, Amsterdam (1981).
29. J. D. Thompson, Magnetic interactions in correlated electron systems: high pressure investigations, in: "Frontiers in Solid State Sciences," L. C. Gupta and M. S. Multani, ed., World Scientific, Singapore (in press).
30. M. Kurisu, T. Takahatake and H. Fujiwara, Gap suppression in CeNiSn under hydrostatic pressure, *Solid State Commun.* 68: 595 (1988).
31. T. Takahatake et al., Formation of an anisotropic energy gap in the valence-fluctuating system in CeNiSn, *Phys. Rev. B* 41: 9607 (1990).

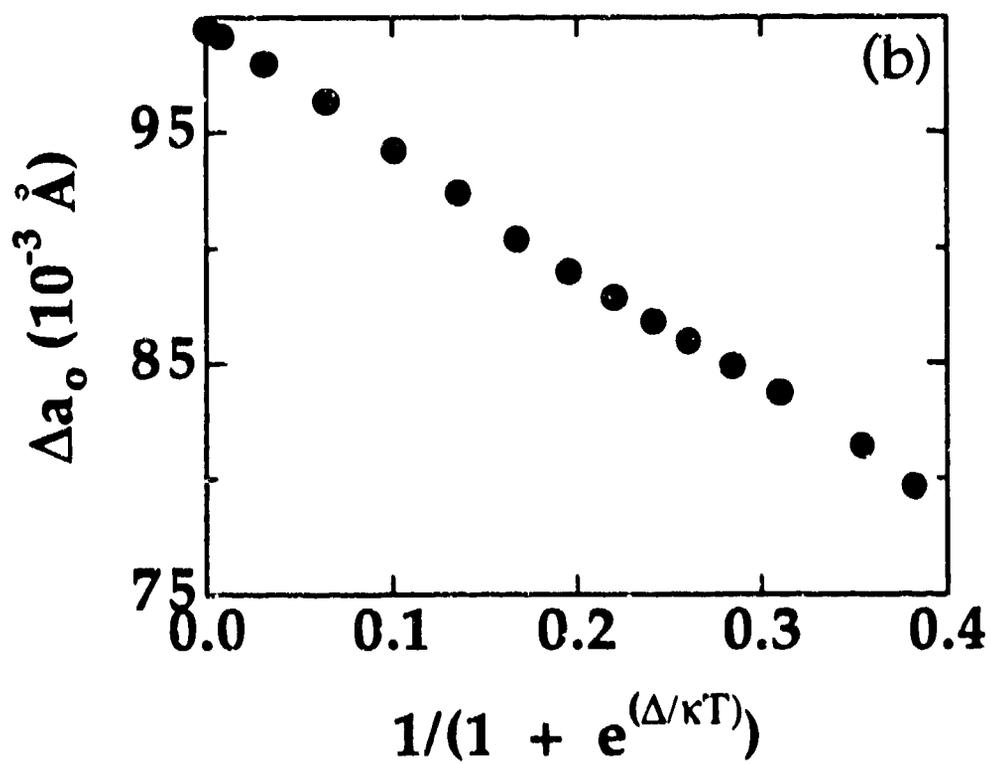
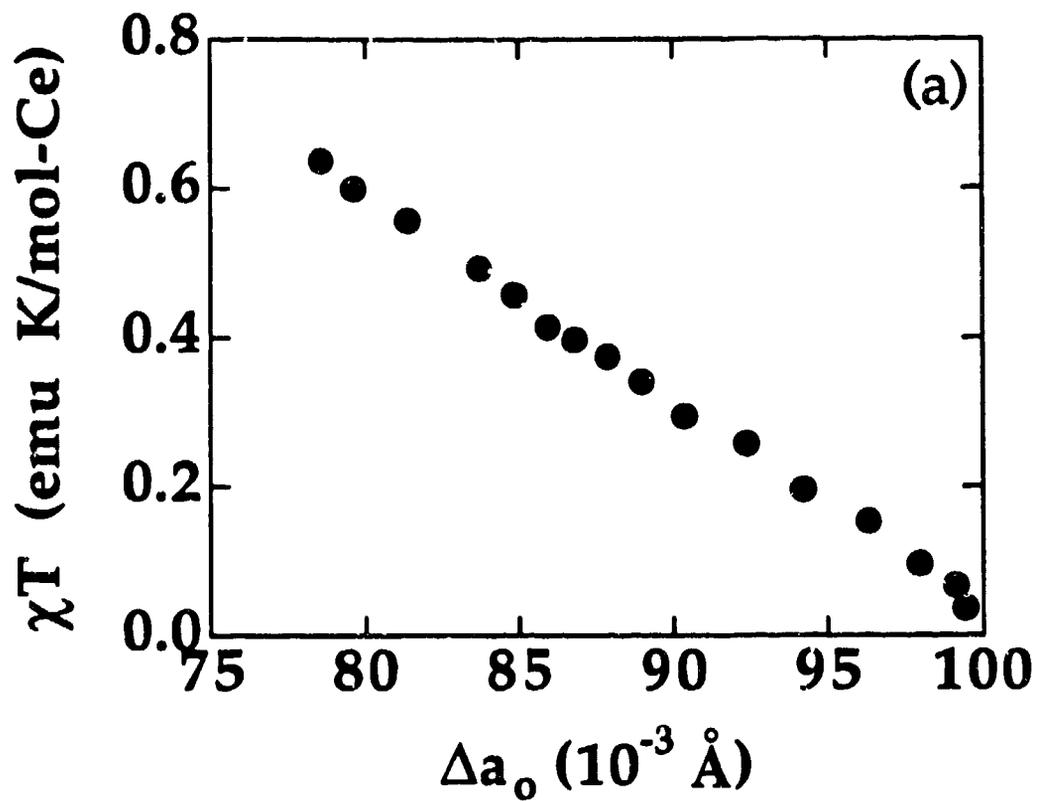
32. F. Iga, M. Kasaya and T. Kasuya, Kondo state in the alloy system  $\text{Lu}_{1-x}\text{Yb}_x\text{B}_{12}$ , *J. Magn. Magn. Mat.* 52: 279 (1985).
33. M. Kasaya et al., Valence instabilities and electrical properties of the La- and Yb-substituted  $\text{SmB}_6$ , in: "Valence Fluctuations in Solids," L. M. Falicov, W. Hanke and M. B. Maple, ed., North-Holland, Amsterdam (1981).
34. P. Schlottmann, Impurity bands in Kondo insulators, *Phys. Rev. B* 46: 998 (1992-II).
35. P. C. Canfield et al., (unpublished).
36. J. M. Lawrence, J. D. Thompson and Y. Y. Chen, Two energy scales in  $\text{CePd}_3$ , *Phys. Rev. Lett.* 54: 2537 (1985).
37. P. C. Canfield et al., Effects of doping on hybridization gapped materials, *J. Magn. Magn. Mat.* 108: 217 (1992); P. C. Canfield et al., Doping and pressure study of  $\text{U}_3\text{Sb}_4\text{Pt}_3$ , *J. Alloys Compds.* 181: 77 (1992).
38. F. Iga, M. Kasaya and T. Kasuya, Specific heat measurements of  $\text{YbB}_{12}$  and  $\text{Yb}_x\text{Lu}_{1-x}\text{B}_{12}$ , *J. Magn. Magn. Mat.* 76 & 77: 156 (1988).
39. P. S. Riseborough, Theory of the dynamic magnetic response of  $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ : a heavy-fermion semiconductor, *Phys. Rev. B* 45: 13984 (1992-II).
40. R. M. Martin and J. W. Allen, Classification of states at the Fermi energy in mixed valence systems, in: "Valence Fluctuations in Solids," L. M. Falicov, W. Hanke and M. B. Maple, ed., North-Holland, Amsterdam (1981).

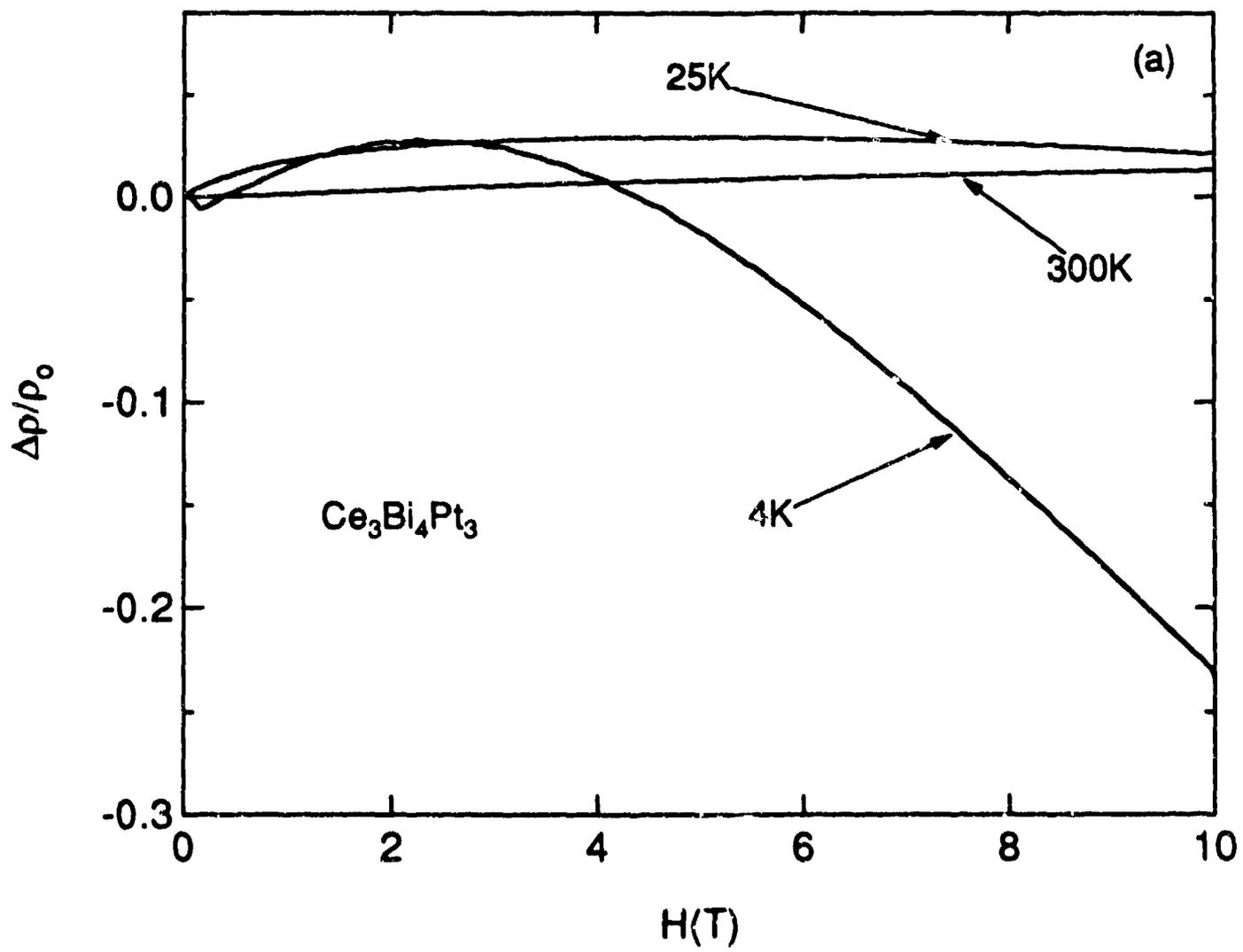












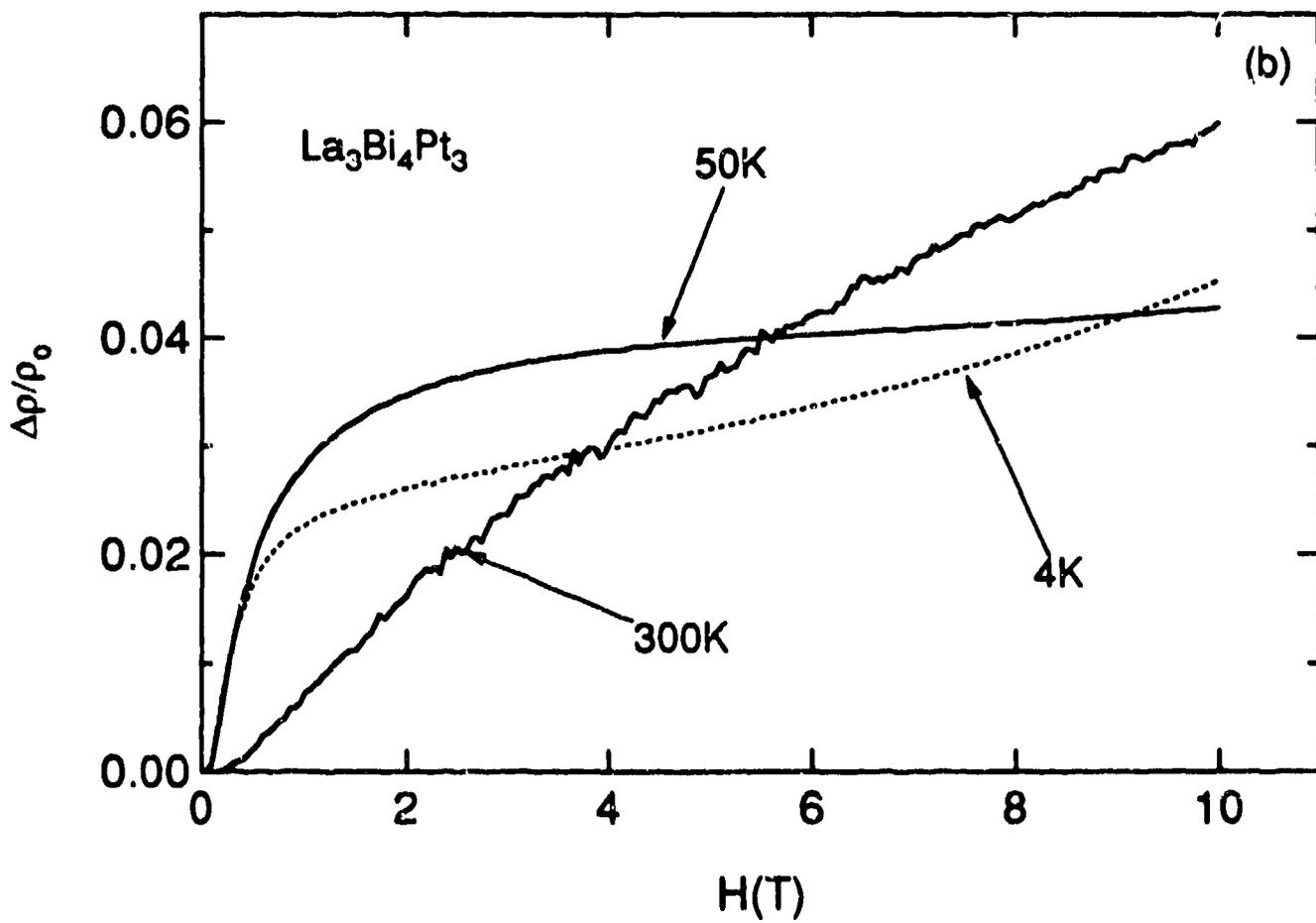


Fig. 6. - temp

