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Hybridization gap in Ce$_3$Bi$_4$Pt$_3$

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We present resistivity $\rho(T)$, susceptibility $\chi(T)$, and specific heat $C(T)$ data for Ce$_3$Bi$_4$Pt$_3$. The susceptibility exhibits a broad maximum centered near 80 K, typical of a somewhat-heavy-electron compound; were the material metallic, a linear coefficient of specific heat $\gamma = 75$ mJ/mol Ce K^2 would be expected. However, the compound is *not* metallic, as indicated by its resistivity which rises to large values at low temperatures and exhibits activated behavior with an activation energy $\Delta/k_B = 35$ K. By analogy to SmB$_6$ and YbB$_{12}$, this energy gap arises from $4f$-electron–conduction-electron hybridization. Due to the gap, electronic excitations are suppressed at low temperatures and the specific heat is smaller than in nonmagnetic La$_3$Bi$_4$Pt$_3$. Alloying with lanthanum ((Ce$_{1-x}$La$_x$)$_3$Bi$_4$Pt$_3$) decreases the resistivity and increases the specific heat towards the value expected for the metallic case; i.e., for moderate alloying ($x = 0.07$) the behavior is that of a moderately disordered heavy-electron metal. We argue that lattice periodicity is an essential requirement for the formation of the hybridization gap.

In heavy-fermion valence-fluctuation compounds, the high-temperature state is believed to consist of a lattice of uncorrelated $4f$ ions, each independently scattering conduction electrons by the Kondo mechanism. At low temperatures correlations exist, and one of two types of coherent ground state can occur. In the vast majority of cases the ground state is metallic (paramagnetic, antiferromagnetic, or superconducting) but in a very limited number of cases [SmB$_6$,[1] YbB$_{12}$,[2-4] CeFe$_4$P$_{12}$ (Ref. 5)] the ground state is insulating with a small energy gap. This gap is believed to arise in a lattice of Kondo impurities from hybridization of the $4f$ and conduction electrons, and hence is called a hybridization gap. We have discovered another rare-earth compound, Ce$_3$Bi$_4$Pt$_3$,[6] which exhibits such small-gap behavior. Here we report thermodynamic behavior and demonstrate the relation of the gap energy to other energy scales (such as the single-ion Kondo temperature). Moderate alloying with lanthanum, which disrupts the lattice periodicity, suppresses the gap and leads to behavior typical of a somewhat-disordered heavy-fermion metal. We compare the thermodynamic behavior to that of other small-gap compounds.

Single crystals of Ce$_3$Bi$_4$Pt$_3$ of typical dimension $1 \times 1 \times 5$ mm^3 were grown out of a Bi flux. The samples have cubic ($I\bar{4}3d$) symmetry,[7] a structure closely related to the Th$_3$P$_4$ type, with lattice constant $a_0 = 9.998 \pm 0.005$ Å. Lanthanum analogs and La-substituted samples were prepared similarly. Susceptibility was measured using a superconducting-quantum-interference-device (SQUID) magnetometer; resistivity utilized a standard four-probe ac technique; specific heat was measured by a time-constant technique.

The magnetic susceptibility of Ce$_3$Bi$_4$Pt$_3$ is shown in Fig. 1 and is compared to that of La$_3$Bi$_4$Pt$_3$. The susceptibility is typical of a somewhat-heavy-electron cerium valence-fluctuation compound: at high temperature it has

Curie-Weiss behavior ($C/T + \Theta$, where C is nearly the $J = \frac{5}{2}$ free-ion value and $\Theta = 125$ K), it has a broad maximum centered at $T_{max} = 80$ K and a finite value $C/\chi(0) = 320$ K as $T \to 0$. (The Curie "tail" is probably extrinsic as it is somewhat sample dependent.) The behavior is similar to that of CeSn$_3$ where $T_{max} = 140$ K.[8] In valence-fluctuation compounds the parameters T_{max}, Θ, and $C/\chi(0)$ vary proportionally to each other.[8] Comparison of Ce$_3$Bi$_4$Pt$_3$ to the case of CeSn$_3$ where $T_{max} = 140$
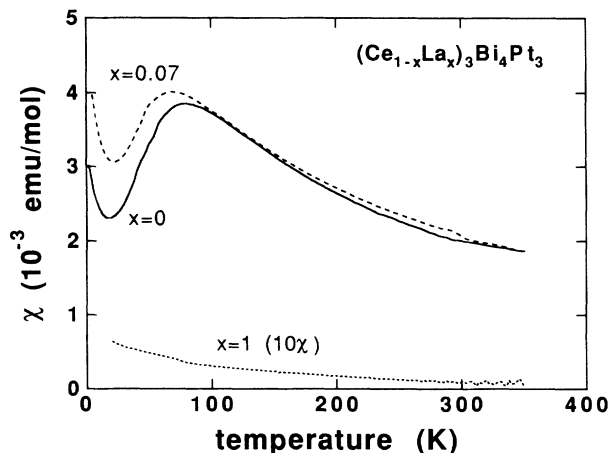
FIG. 1. The susceptibility measured in a 0.1 T field of Ce$_3$Bi$_4$Pt$_3$ (solid curve) compared to that of La$_3$Bi$_4$Pt$_3$ (dotted line) and (Ce$_{1-x}$La$_x$)$_3$Bi$_4$Pt$_3$ (dashed line) for $x = 0.07$. The vertical axis is normalized per mole of Ce for $x = 0$ and 0.07 and per mole of La for $x = 1.0$. Data for $x = 0.035$ (not shown) fall intermediate to $x = 0$ and $x = 0.07$. The susceptibility of Ce$_3$Bi$_4$Pt$_3$ is typical of valence fluctuation compounds. As expected from its cubic symmetry, the magnitude, and temperature dependence of χ for Ce$_3$Bi$_4$Pt$_3$ was unchanged for fields applied along different crystallographic orientations.

K, $\Theta \cong 220$ K, and $C/\chi(0) = 475$ K shows that both have similar ratios of T_{max}:Θ:$C/\chi(0)$. Such scaling laws are predicted by Kondo-ion theories such as Bethe-ansatz calculations,[9] which also give the relation between T_{max} and the linear coefficient of specific heat γ for various orbital degeneracies. On the basis of Bethe-ansatz theory, we would expect γ to be 75 mJ/mol Ce K^2 for metallic Ce₃Bi₄Pt₃. Because γ scales inversely with T_{max}, we also could use the observed values of γ and T_{max} (50 mJ/mol Ce K^2 and 140 K) for CeSn₃ (Ref. 8) to arrive at a similar estimate.

Figure 2(a) compares C/T for Ce₃Bi₄Pt₃ with that of the nonmagnetic analog La₃Bi₄Pt₃. Instead of the moderately large γ expected from Bethe-ansatz analysis of the susceptibility, we find that γ for Ce₃Bi₄Pt₃ is only 3.3 mJ/mol Ce K^2, a value even smaller than that of La₃Bi₄Pt₃ ($\gamma = 10$ mJ/mol La K^2). Not only is γ of Ce₃Bi₄Pt₃ small, but as will be argued, we believe that this small γ is not intrinsic and that in the absence of extrinsic contributions it should be zero.

The notable absence of an appreciable electronic contribution to the specific heat arises because Ce₃Bi₄Pt₃ is nonmetallic at low temperatures, as shown in Fig. 3(a). Above ~ 100 K, $\rho(T) \propto \exp(\Delta/k_B T)$ with activation energy $\Delta/k_B = 35$ K or $\Delta = 3$ meV. In this temperature range $k_B T$ exceeds Δ so that the apparent value of Δ/k_B cannot be taken at face value. However, we note that analysis of
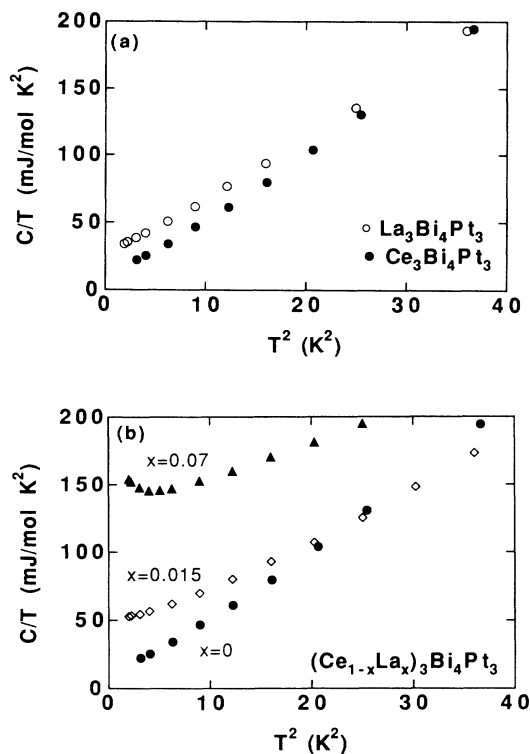

FIG. 2. (a) Specific heat per formula unit mole divided by temperature C/T for Ce₃Bi₄Pt₃ and La₃Bi₄Pt₃ for T below 7 K. The linear term is very small for Ce₃Bi₄Pt₃, consistent with nonmetallic behavior. (b) C/T per formula unit mole for (Ce₁₋ₓLaₓ)₃Bi₄Pt₃. On alloying an enhanced coefficient of specific heat occurs, as expected for disordered metallic behavior.
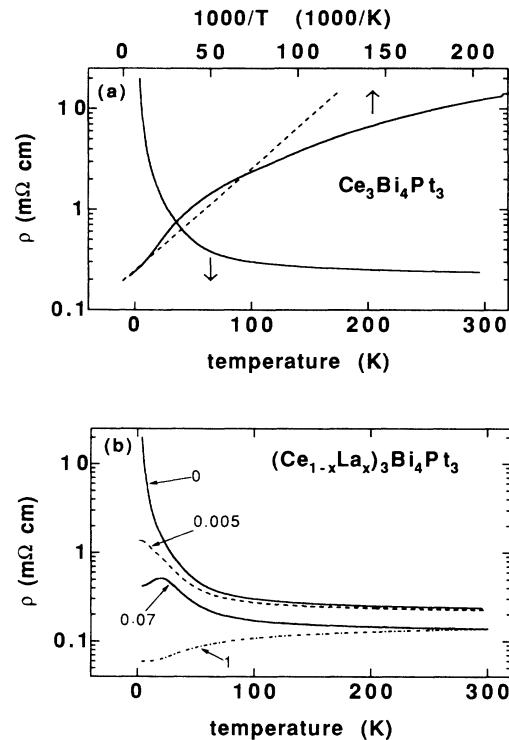

FIG. 3. (a) The logarithm of the resistivity of Ce₃Bi₄Pt₃ vs temperature T and inverse temperature $1000/T$. The dashed line represents activated behavior with activation energy $\Delta/k_B = 35$ K derived from a fit to $T > 50$ K data. (b) Resistivity vs temperature for (Ce₁₋ₓLaₓ)₃Bi₄Pt₃ for several values of x given in the figure. The resistivity for $x = 0.07$ is typical of a moderately disordered valence-fluctuation metal.

the temperature-dependent Seebeck and Hall coefficients[10] implies a similar value for Δ/k_B and that $\rho(T)$ increases sharply below ~ 50 K, and exceeds at lower temperature any reasonable upper limit (due to scattering) for a metal. Clearly, a gap on the order of 35 K develops in Ce₃Bi₄Pt₃ and we adopt this value for discussion purposes. Below about 30–50 K the activated resistivity tends towards saturation and the Hall constant also deviates from its activated behavior. The low-temperature transport behavior, we believe, is dominated by extrinsic effects.

There are thus two intrinsic energy scales—the high-temperature single-ion Kondo temperature and the activation energy. The definition of the former is somewhat theory dependent; in Bethe-ansatz theory it would be $4T_{max}$ or about 320 K for Ce₃Bi₄Pt₃. The gap temperature is $T_{gap} = \Delta/k_B = 35$ K. The extrinsic effects set in when the temperature satisfies $T \lesssim T_{gap}$.

Because the ground state is not metallic, the electronic contribution to the specific heat should vanish at temperatures smaller than T_{gap}. This explains why the specific heat of Ce₃Bi₄Pt₃ is even smaller than that of La₃Bi₄Pt₃. For $T < 20$ K the specific heat is essentially dominated by lattice effects (we estimate the Debye temperature of Ce₃Bi₄Pt₃ to be ~ 170 K); the small linear term is sample dependent, ranging from (3–5 mJ/mol Ce K^2), and we believe it arises from the same extrinsic cause as the low-

temperature deviations in the transport behavior and the Curie tail in susceptibility.

Alloying with lanthanum $((Ce_{1-x}La_x)_3Bi_4Pt_3)$ disrupts the lattice periodicity of magnetic Ce ions but causes very little change in the susceptibility, as shown in Fig. 1. In contrast, the specific heat increases dramatically with La substitution and for $x = 0.07$ the linear specific-heat coefficient has increased to $\gamma = 45$ mJ/mol Ce K^2 [see Fig. 2(b)]. Accompanying the change in C/T [Fig. 3(b)], the resistivity also decreases dramatically. At $x = 0.07$ the resistivity is similar to the resistivity of $Ce_{1-x}La_xPd_3$ for $x = 0.07$ in overall shape and magnitude.[11] The observed value of γ is also a significant fraction of the value expected for a metallic Ce compound with $T_{max} = 80$ K. Thus, modest alloying destroys the activated behavior and instead gives behavior typical of a metallic valence-fluctuation compound with a similar degree of disorder.

Together, these substitutional studies indicate the nature of the small gap in pure $Ce_3Bi_4Pt_3$. Aside from the very weak, monotonic depression of T_{max} with La substitution, the overall temperature dependence of χ is virtually unchanged, indicating at most a minor decrease in the characteristic high-temperature energy scale. This is understood straightforwardly since the Bethe ansatz, from which scaling laws for T_{max}, Θ, and $C/\chi(0)$ derive, is simply a single-ion theory, i.e., conclusions from it are independent of lattice periodicity. Consequently, small substitutions for Ce should not affect the susceptibility provided the ground-state degeneracy is not lifted, as appears to be the case. At the same time, Bethe ansatz predicts that γ also should not change for the same reason. However, it does and the change is accompanied by suppression of the energy gap. The drastic decrease in $\rho(T)$ clearly is not a simple impurity, i.e., single-ion, effect but results from the disruption of translational invariance of the Ce sublattice. Similar "coherence" effects that arise from interactions among periodically placed Kondo impurities are found in metallic mixed-valence and heavy-electron systems where even minor lattice-symmetry breaking leads to large changes in low-temperature resistivity (in these cases to an increase in the resistivity); $Ce_{1-x}La_xPd_3$ mentioned above is a prime example. This argument leads directly to the conclusion that the gap in $Ce_3Bi_4Pt_3$ is made possible by the same requirement of lattice periodicity necessary for coherence in metallic systems. That the Bethe-ansatz estimate for γ is essentially recovered for 7% La substitution indicates that γ is essentially a single-ion effect, once the gap in the density of states is suppressed.

Anderson[12] has suggested that the temperature scale T_{coh} on which coherence develops differs from the single-ion scale by a factor of $N = 2J + 1$, where J is the orbital degeneracy. More recent theories[13] based on $1/N$ expansions support this idea. We have estimated the single-ion scale to be crudely $4T_{max}$ from Bethe ansatz. Taking $J = \frac{5}{2}$ for Ce^{3+} gives $T_{coh} = 50$ K, which, perhaps fortuitously, is rather close to the estimate for $\Delta/k_B = 35$ K. Taking this agreement at face value supports the argument for the importance of coherence effects in the appearance of a hybridization gap in $Ce_3Bi_4Pt_3$.

Some evidence supporting this argument is found in YbB_{12}, which has physical characteristics very similar to $Ce_3Bi_4Pt_3$. For both compounds, the resistivity is activated with an activation energy of ~ 3 meV,[2] the susceptibility maximum occurs at 75 K, and the Hall constant exhibits[3] activated behavior. The specific heat[4] is small at low temperatures and modest alloying $(x \approx 0.07$ for $(Ce_{1-x}La_x)_3Bi_4Pt_3$ or for $Yb_{1-x}Lu_xB_{12})$ increases γ to ~ 50 mJ/mol R K^2, where R represents the rare-earth element. Because $J = \frac{7}{2}$ for Yb^{3+}, the estimate for $T_{coh} \approx 38$ K is somewhat smaller than in $Ce_3Bi_4Pt_3$ but still close to Δ/k_B.

Finally, there is $CeFe_4P_{12}$, which has a low-temperature susceptibility at least ten times smaller than that of $Ce_3Bi_4Pt_3$ but has an activation energy $\Delta/k_B \cong 1500$ K that is much larger.[5] Because the single-ion temperature is proportional to the inverse of the $4f$ contribution to $\chi(0)$, this comparison suggests that Δ/k_B increases as the single-ion temperature increases. This is precisely the behavior expected from the relationship $\Delta/k_B \propto T_{coh} \propto 4T_{max}/(2J + 1)$.

A possible alternative to this interpretation is that a metallic impurity band forms with La substitution and that it is responsible for suppressing $\rho(T)$ at low temperatures. Analysis of the transport properties of La- and Yb-substituted SmB_6 has invoked such an interpretation.[14] However, it is difficult to understand how such a large γ could develop in this band, given the small number of carriers implied by the small La substitutions in $Ce_3Bi_4Pt_3$. Further, it would seem quite fortuitous that a two-band model would give a similar relationship between Δ/k_B and T_{max} in the three rather-electronically-disparate systems discussed above; whereas, coherence effects predict this relationship explicitly.

In summary, $Ce_3Bi_4Pt_3$ is one of the few examples of a Ce-based intermetallic with a hybridization gap. We argue that lattice periodicity is an essential requirement for the formation of this gap, and that once it is suppressed, single-ion effects dominate both the magnetic susceptibility and electronic specific heat, as is expected from a Bethe-ansatz theory of a lattice of noninteracting Kondo impurities. Moreover, we tentatively identify the gap with the development of coherence resulting from interactions among the periodically placed Kondo impurities. Why a hybridization gap at the Fermi energy should appear in so few compounds remains unanswered but may be related to the cubic structure common to known examples. Further insight into the microscopic interactions responsible for the gap may be found in NMR, neutron-scattering, and high-pressure experiments. Optical or tunneling spectroscopy should determine the gap directly and its change with Ce substitutions.

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