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Effects of doping on hybridization gapped materials

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Doping studies are presented on three materials exhibiting hybridization gaps: $Ce_3Bi_4Pt_3$, $U_3Sb_4Pt_3$ and CeRhSb. In the case of trivalent La, Y, or Lu substituting for Ce or U, there is a suppression of the low temperature gap and an increase in the electronic specific heat, γ. In the case of tetravalent Th substitutions for U there is no change in γ and in the case of tetravalent Zr substitution for Ce in CeRhSb, there is an enhanced semiconductor-like behavior in the electrical resistance. These results are discussed in the light of a simple model of hybridization gapped systems.

In the past year materials exhibiting a hybridization gap at low temperatures have reemerged as subjects of great experimental and theoretical interest. $Ce_3Bi_4Pt_3$ [1-3], $U_3Sb_4Pt_3$ [4,5] and recently CeRhSb [6] have been found to exhibit gaps of approximately 50, 200 and 10 K respectively. By replacing Ce or U by tri- and tetravalent dopants, the nature of the low temperature ground state can be probed as well as the sensitivity of the hybridization gap to electron count.

Both cubic compounds, $Ce_3Bi_4Pt_3$ and $U_3Sb_4Pt_3$, were single crystals grown from Bi and Sb fluxes, respectively, while CeRhSb was arc-melted in an Ar atmosphere in a procedure similar to that described in ref. [6]. The materials were characterized by standard four-probe electrical resistance, dc magnetic susceptibility using a SQUID magnetometer, and by specific heat, using a small mass calorimeter.

Fig. 1 shows the electrical resistivity of both $Ce_3Bi_4Pt_3$ and $U_3Sb_4Pt_3$ as a function of temperature as well as the temperature dependent magnetic susceptibility of $Ce_3Bi_4Pt_3$ (inset). Arrhenius plots of $Ce_3Bi_4Pt_3$ [1] and $U_3Sb_4Pt_3$ [5] resistance data lead to

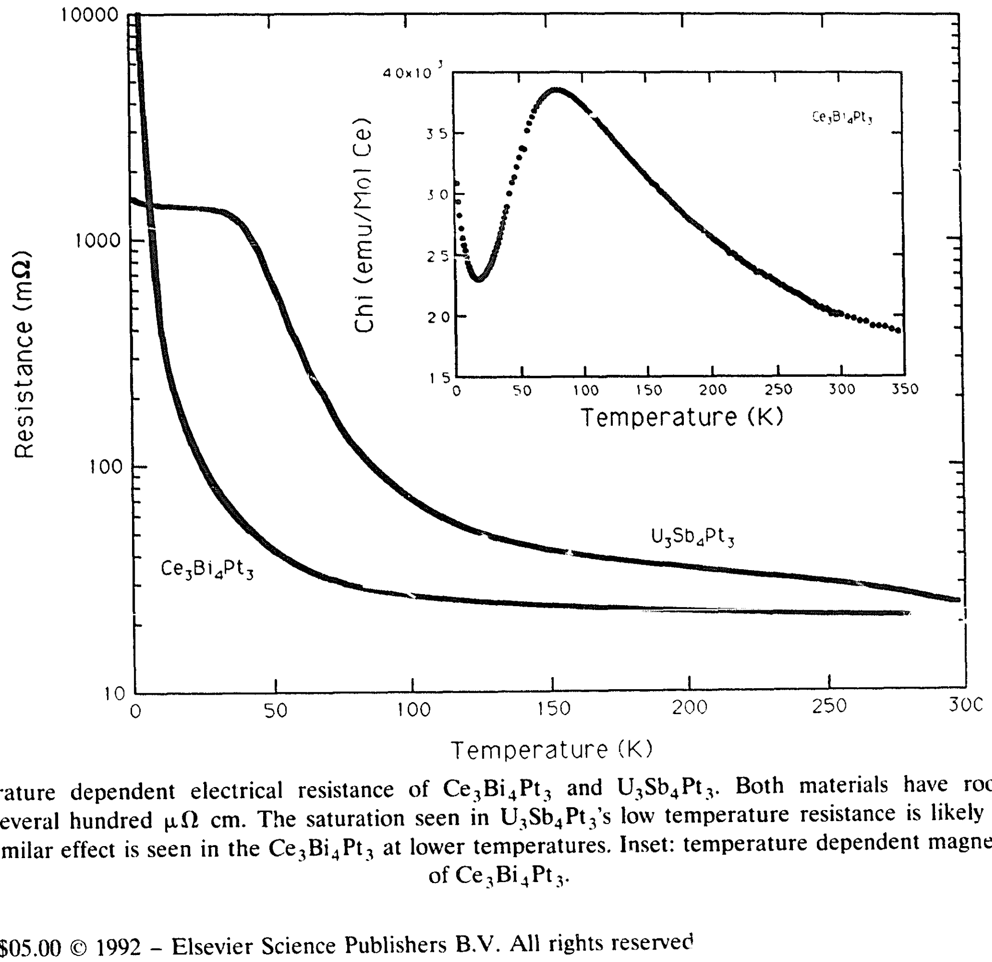

Fig. 1. Temperature dependent electrical resistance of $Ce_3Bi_4Pt_3$ and $U_3Sb_4Pt_3$. Both materials have room temperature resistivities of several hundred μΩ cm. The saturation seen in $U_3Sb_4Pt_3$'s low temperature resistance is likely due to impurity conduction; a similar effect is seen in the $Ce_3Bi_4Pt_3$ at lower temperatures. Inset: temperature dependent magnetic susceptibility of $Ce_3Bi_4Pt_3$.

the gaps mentioned above, and the magnetic susceptibility of $Ce_3Bi_4Pt_3$ is that of a canonical Ce mixed valence system with a maximum found at $T_{MAX} = 80$ K. The substitution of La for Ce in $Ce_3Bi_4Pt_3$ [1,2] leads to a suppression of the electrical resistance over all temperatures, a decrease of T_{MAX}, and an increase in the electronic specific heat at low temperatures (fig. 2a). Substitutions of Th, Y, and Lu for U in $U_3Sb_4Pt_3$ [5] cause a similar decrease in resistance, but only the Y and Lu give rise to a similar increase in γ (fig. 2b).

In fig. 3, electrical resistance data for CeRhSb doped with Zr and La are plotted as a function of temperature [7]. In the pure material there is a high temperature maximum at $T = 125$ K and a minimum at $T = 13$ K followed by a factor of 5 increase in resistance down to 1.2 K. If the gap is evaluated below 7 K, a gap of approximately 7 K is found over a limited region. With the substitution of La for Ce, the high temperature behavior is qualitatively unchanged, but the low temperature, gapped behavior is suppressed. This is similar to what is seen in La doped $Ce_3Bi_4Pt_3$ [2,8] where the high temperature resistance does not change significantly, but the low temperature activated behavior is suppressed rapidly by the addition of La. The substitution of Zr for Ce leads to a very different behavior. In addition to a factor of three increase in the room temperature resistivity, the resistivity increases monotonically over the whole temperature region, making the sample more semiconductor-like.

There are two distinct features of these systems that can be seen as a result of these doping studies. One is shown in fig. 2c where γ is plotted as a function of $1/T_{MAX}$. At dopings high enough to have destroyed the low-temperature, gapped state, γ approaches the value the Coqblin–Schrieffer model predicts for the measured value of T_{MAX} [9]. This implies that as the system becomes metallic at low temperatures, the Ce acts like a $J = 5/2$ impurity dissolved in a metallic host.

The second feature of these systems that becomes apparent with doping is that there is a large difference between doping with a tri- or tetravalent dopant. In fig. 2b it can be seen that doping $U_3Sb_4Pt_3$ with trivalent Y and Lu leads to an increase in γ, in a similar manner as doping with trivalent La leads to an increase in the γ of $Ce_3Bi_4Pt_3$; but doping $U_3Sb_4Pt_3$ with tetravalent Th causes no rise whatsoever. In a related manner, fig. 3 shows that doping CeRhSb with trivalent La suppresses the gap at low temperatures, but does not significantly change the high temperature resistivity. Tetravalent Zr, on the other hand, causes a dramatic change in both the absolute value and the temperature dependence of the resistivity. In all of these cases the addition of trivalent dopants causes the suppression of the low-temperature, gapped state with little change in the higher temperature resistance, and enhances γ. On the other hand, the addition of tetravalent Th to $U_3Sb_4Pt_3$ leads to no increase in γ and the addition of tetravalent Zr to CeRhSb leads to a more semiconductor-like temperature dependent resistivity.

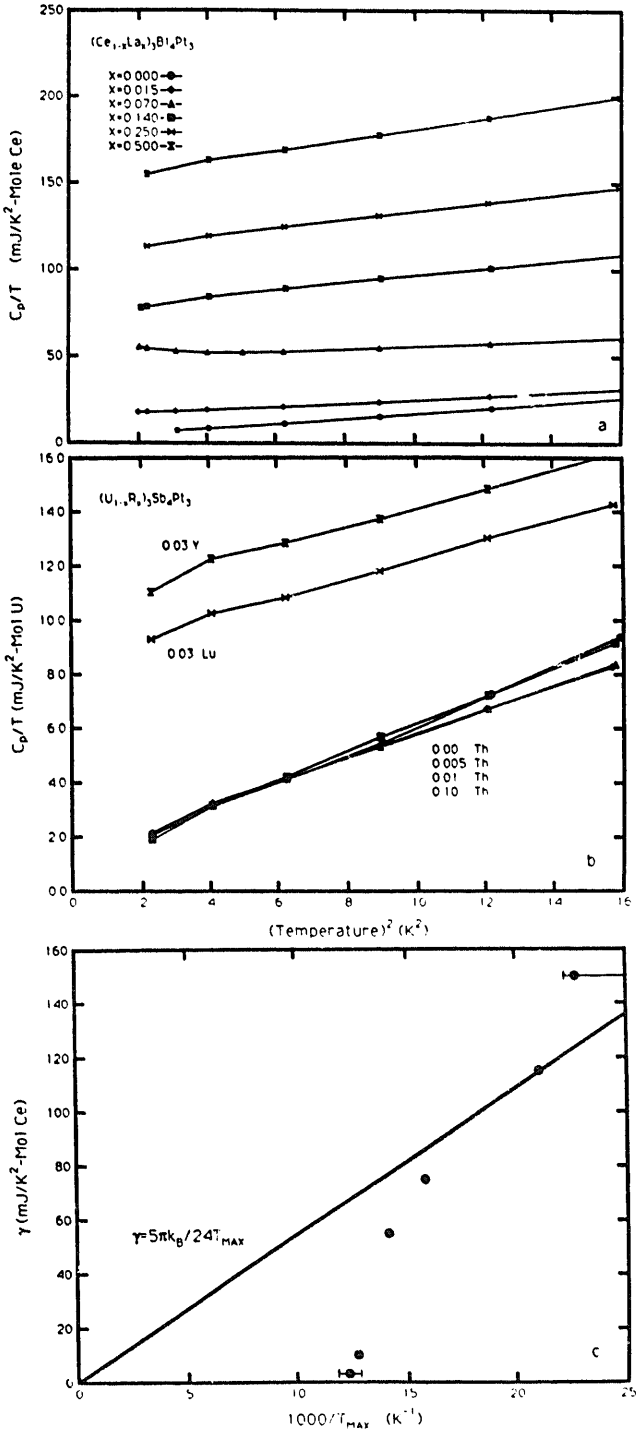

Fig. 2. (a) C/T vs. T^2 for pure and doped $Ce_3Bi_4Pt_3$. (b) C/T vs. T^2 for pure and doped $U_3Sb_4Pt_3$. (c) C/T vs. $1/T_{MAX}$ for $Ce_3Bi_4Pt_3$. Error bars indicate degree of uncertainty in determining T_{MAX}. Solid line is C/T predicted by ref. [9].

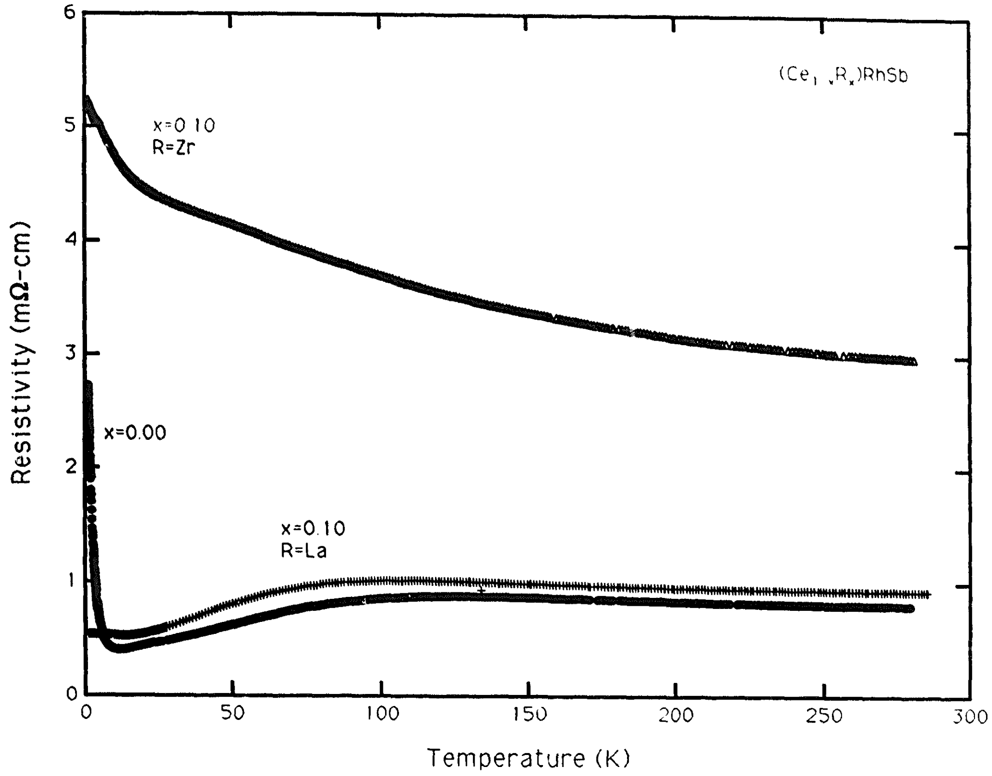

Fig. 3. Temperature dependent electrical resistivities of pure and doped CeRhSb.

One possible explanation for this body of data and the general rarity of systems that exhibit hybridization gaps is that they require an electronic system with a fundamentally simple bandstructure. In order for the hybridization of the f-band with the conduction band to lead to a fully gapped system there cannot be more than one band crossing the Fermi surface before the hybridization is turned on [10]. This underlying simplicity of bandstructure makes it very easy to envisage a nearby semiconductor that can be found by changing the filling of the band. This is the direction that tetravalent dopants seem to be moving the system. On the other hand, the trivalent dopants seem to only changing the nature of the system slightly, suppressing the low temperature gap and giving rise to the increased γ. In this picture this would seem to indicate that the valence of the Ce/U at low temperatures is still [11] close to 3^+, which is consistent with recent neutron scattering results [12].

In summary, we have reviewed the results of tri- and tetravalent doping on three hybridization gapped systems: $Ce_3Bi_4Pt_3$, $U_3Sb_4Pt_3$ and CeRhSb. Trivalent doping leads to metalization and behavior expected for f-moments dissolved in a metallic host, but tetravalent doping leads to a more semiconductor-like behavior.

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References

[1] M.F. Hundley, P.C. Canfield, J.D. Thompson, Z. Fisk and J.M. Lawrence, Phys. Rev. B 42 (1990) 6842

[2] M.F. Hundley, P.C. Canfield, J.D. Thompson, Z. Fisk and J.M. Lawrence, Physica B (in press).

[3] A. Severing, J.D. Thompson, P.C. Canfield, Z. Fisk and P. Riseborough, Phys. Rev. B (submitted).

[4] T. Takabatake, S. Miyata, H. Fujii, Y. Aoki, T. Suzuki, T. Fujita, J. Sakurai and T. Hiraoke, J. Phys. Soc. Jpn. 59 (1990) 4412.

[5] P.C. Canfield, A. Lacerda, J.D. Thompson, G. Sparn, W.P. Beyermann, M.F. Hundley and Z. Fisk, J. Less-Common Met. (submitted).

[6] S.K. Malik and D.T. Adroja, Phys. Rev. B 43 (1991) 6277.

[7] For both La and Zr doping 5% levels are intermediate between the pure and 10% doping. These data have been left out of the plot for clarity.

[8] P.C. Canfield, M.F. Hundley, J.D. Thompson, A. Lacerda and Z. Fisk, unpublished.

[9] V.T. Rajan, Phys. Rev. Lett. 51 (1983) 308.

[10] Stuart Trugman, private communication.

[11] Susceptibility data in refs. [1–6] are consistent with trivalent Ce/U at high temperatures.

[12] G. Kwei, J.M. Lawrence, P.C. Canfield, W.P. Beyermann, J.D. Thompson, A.C. Lawson and J.A. Goldstone, Phys. Rev. B (submitted).