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Doping and pressure study of $U_3Sb_4Pt_3$

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Abstract

The effects of doping and pressure on the $U_3Sb_4Pt_3$ system have been studied. Substitution of either trivalent yttrium or lutetium for uranium causes significant changes in the temperature dependences of the electrical resistance and of the magnitude of the linear coefficient of the specific heat γ. However, substitution of tetravalent thorium causes little change in γ, even though it affects the electrical resistance in a manner similar to that seen in the cases of lutetium and yttrium. Finally, application of hydrostatic pressures up to 16.5 kbar causes no significant change in the electronic gap deduced from the electrical resistance.

1. Introduction

Recent work on the cubic $Ce_3Bi_4Pt_3$ system [1] has shown that it appears to be a semiconducting mixed valence system with an energy gap of approximately 50 K in its electronic spectrum. In addition to this, doping studies of this system [2, 3] indicate that as the low temperature gap is destroyed by lanthanium substitution for cerium, the system recovers the electronic specific heat that would be expected for a metallic mixed valence system having a comparable characteristic energy scale [2]. Application of pressures up to approximately 20 kbar on the $Ce_3Bi_4Pt_3$ system causes the gap seen in the electrical resistance to open further, which is opposite from the pressure dependence of the gap seen in SmB_6 [4] and CeNiSn [5], two other examples of gapped, mixed valence systems.

The $U_3Sb_4Pt_3$ system is isostructural with $Ce_3Bi_4Pt_3$ and has a gap of roughly 200 K. This system has been reported by Takabatake *et al.* [6, 7] and Takegahara *et al.* [8] in its pure form as part of a larger study of the $U_3Sb_4T_3$ (T≡Ni, Cu, Pd, Pt, Au) systems, but a detailed investigation of the stability of the gap with respect to substitutions and pressure was not made. As will be shown, the effect of substitutions and pressure on the properties of $U_3Sb_4Pt_3$ are similar to those found in the cerium analogue, but because the uranium system supports a wider variety of dopants, we are able to extend our knowledge of these gapped systems.

2. Experimental methods

Pure $U_3Sb_4Pt_3$ single crystals and crystals doped with tetravalent thorium and trivalent lutetium and yttrium were grown from an antimony flux*. The electrical resistance measurements were performed with a lock-in amplifier using a four-probe configuration, the magnetic susceptibility was measured using a Quantum Design SQUID susceptometer and the specific heat measurements were done using a relaxation method in a small mass calorimeter. The electrical resistance measurements under hydrostatic pressure were performed using a self-clamping pressure cell that has been described earlier [9].

3. Results and discussion

Figure 1 shows the temperature dependence of the electrical resistance at three representative pressures; the inset shows the temperature dependence of the magnetic susceptibility at atmospheric pressure. The resistance at atmospheric pressure is in qualitative agreement with the data shown by Takabatake *et al.* [6], showing a gap of approximately 200 K between 50

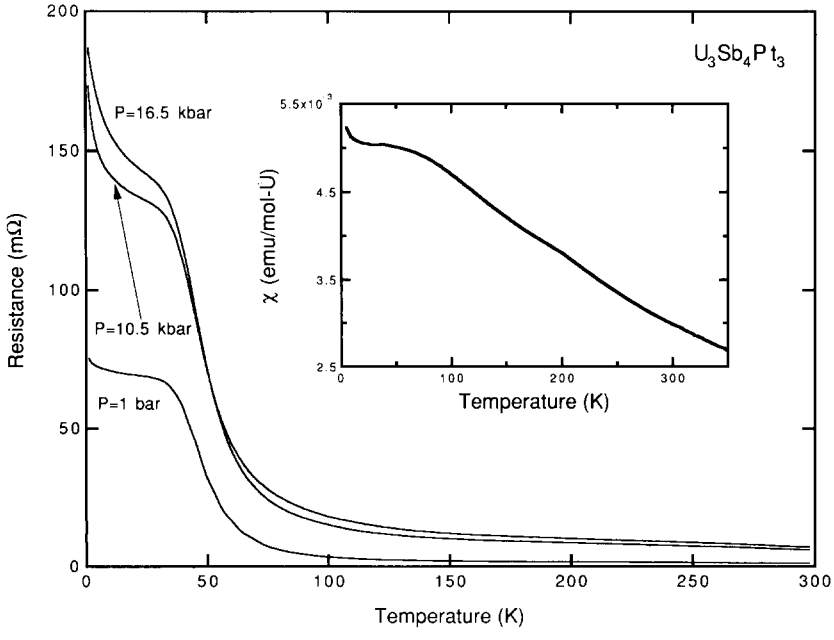

Fig. 1. Resistance *vs.* temperature of $U_3Sb_4Pt_3$ at 1 bar, 10.5 and 16.5 kbar. Inset: magnetic susceptibility *vs.* temperature of $U_3Sb_4Pt_3$ at 1 bar.

*The doping levels cited in this paper represent the ratio of uranium to dopant dissolved in the flux. In the lanthanum-doped $Ce_3Bi_4Pt_3$ samples the nominal doping levels were borne out by both elemental analysis and magnetic susceptibility measurements.

and 150 K and a gap of approximately 500 K above 250 K. The magnetic susceptibility is Curie–Weiss like from 350 to below 200 K with a paramagnetic $\theta = -160$ K and an effective moment $\mu_{eff} = 3.3\ \mu_B$, which is close to the value for either U^{3+} or U^{4+}. In this respect $U_3Sb_4Pt_3$ is unlike $Ce_3Bi_4Pt_3$ where only the trivalent state of cerium carries a magnetic moment. Given the similarities between $U_3Sb_4Pt_3$ and $Ce_3Bi_4Pt_3$, it is very likely that uranium is mixed valent between U^{3+} and U^{4+} with the valence changing from U^{3+} at high temperature toward U^{4+} as the temperature is reduced.

As pressure is applied to $U_3Sb_4Pt_3$, the resistance increases at all temperatures; however, given the jump in room temperature resistance between 1 bar and 10.5 kbar, it is not clear whether this is intrinsic or simply the result of a change in the effective cross-section of the sample (sample cracking). The gap does not change significantly, which is in contrast to the factor-of-3 increase in the gap of $Ce_3Bi_4Pt_3$ from 50 K at 1 bar to 180 K at 16.5 kbar [10]. This is different from both SmB_6 [4] and CeNiSn [5] in which the gap decreases with the application of pressure.

Figure 2 shows the temperature dependence of the electrical resistance of various dopings of $U_3Sb_4Pt_3$. The room temperature resistivities of all of these samples are within a factor of 3 of 25 mΩ cm. (Because these are all irregularly shaped single crystals, this uncertainty arises solely from the accuracy with which we can estimate the sample dimensions.) Even 1% substitutions for uranium depress the low temperature rise in the resistance

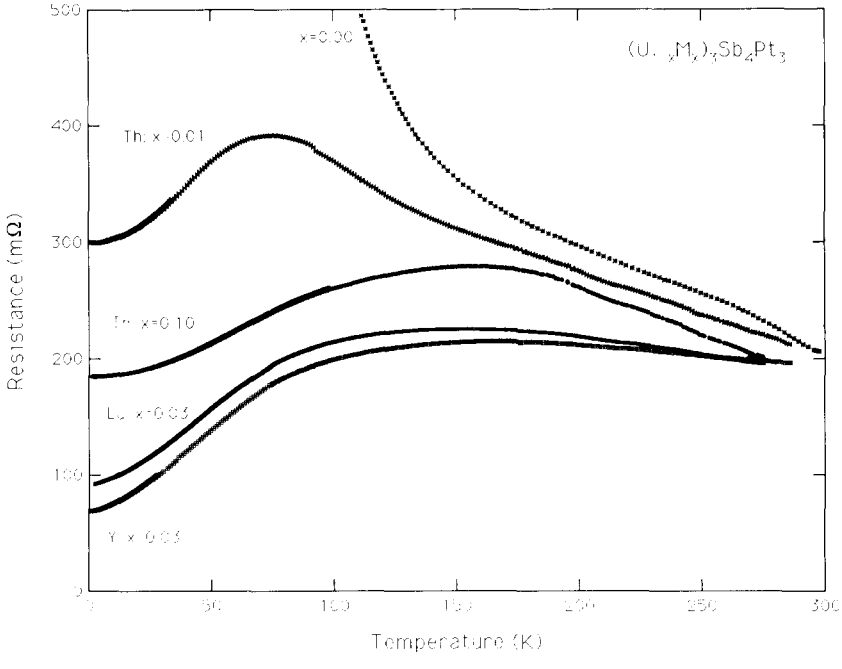

Fig. 2. Resistance *vs.* temperature of doped $U_3Sb_4Pt_3$. All samples have roughly the same room temperature resistivity of 25 mΩ cm.

and produce a resistance maximum at temperatures between 50 and 200 K. The temperature dependences of the thorium-, lutetium- and yttrium-doped samples all follow the trend that the temperature of this resistive maximum moves up with higher doping concentrations. It is also worth noting that $U_3Sb_4Pt_3$ is more sensitive to doping than $Ce_3Bi_4Pt_3$. At 25% La doping, $Ce_3Bi_4Pt_3$ shows much more of a semiconductor-like, temperature-dependent resistance than the 10% Th-doped $U_3Sb_4Pt_3$ sample.

In Fig. 3 we plot the specific heat divided by temperature *vs.* temperature squared. The pure material and three thorium dopings all show virtually the same behavior, whereas the 3% Lu and Y dopings show enhanced electronic specific heats γ. The electronic specific heat increasing with trivalent dopant concentration is precisely what is seen in the $(Ce_{1-x}La_x)_3Bi_4Pt_3$ system [2, 3]. In that case the addition of lanthanum causes γ to rise from approximately 0 to 150 mJ K^{-2} (mol Ce)$^{-1}$ with 50% La substitution.

The fact that thorium doping does not cause a rise in the electronic specific heat of $U_3Sb_4Pt_3$ but the yttrium and lutetium dopings do is a very interesting result. It is worth noting that of the dopants used, thorium is the only one that is tetravalent. Various tetravalent dopings have been tried in the $Ce_3Bi_4Pt_3$ system, but, using our flux growth techniques, neither thorium, zirconium nor hafnium go in. The lack of γ enhancement with tetravalent doping is a feature of this system that must be accounted for in

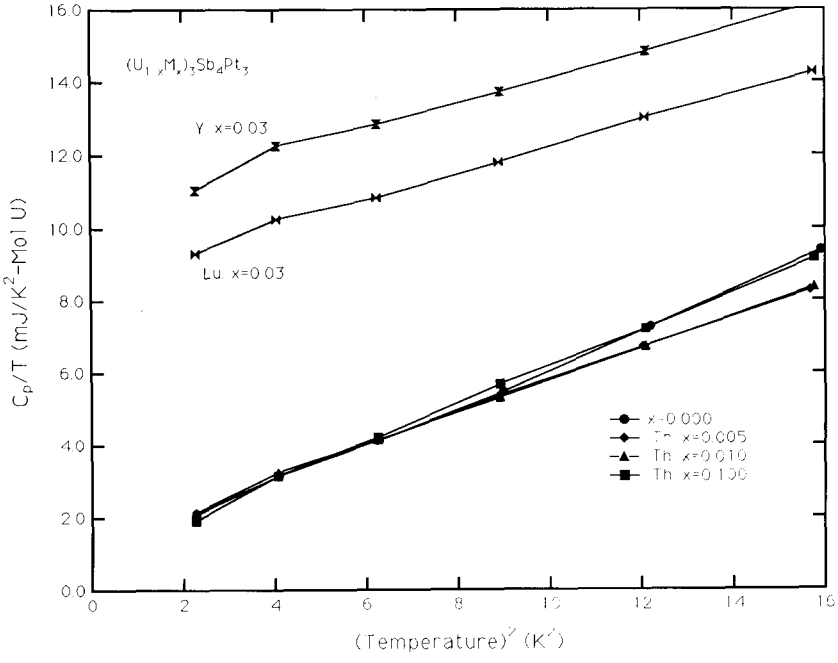

Fig. 3. Specific heat divided by temperature *vs.* temperature squared for doped $U_3Sb_4Pt_3$ samples. The pure and three thorium-doped samples all have similar behavior.

any attempt to model these systems theoretically and to date may be the most important clue as to the origin of the gap in these materials.

It is worth noting that there is an isostructural system in which both the uranium and thorium members have been examined: $U_3Sb_4Ni_3$ and $Th_3Sb_4Ni_3$ [6]. The reported gaps for the uranium and thorium members of this family are 0.20 and 0.07 eV respectively. This seems to indicate that the uranium is not tetravalent at low temperatures and that the gap that is seen is at least in part due to electron correlation effects. Unfortunately we have been unable to grow $Th_3Sb_4Pt_3$.

4. Summary

We have performed pressure and doping studies of the $U_3Sb_4Pt_3$ system. There is very little change in the electrical resistance of $U_3Sb_4Pt_3$ up to pressures of 16.5 kbar as might be expected from the large gap value relative to that in $Ce_3Bi_4Pt_3$, CeNiSn or SmB_6. Doping with the trivalent ions of lutetium and yttrium causes a change in the electrical resistance and also leads to an enhancement of the electronic specific heat. On the other hand, doping with tetravalent thorium does not cause any change in the electronic specific heat, even though the change in the electrical resistance is comparable to that seen with the trivalent dopings.

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