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$Ce_3Cu_xPt_{3-x}Sb_4$: Modifying the properties of a Kondo insulator by substitutional doping

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The temperature dependence of the magnetic susceptibility, thermopower, and electrical resistivity were explored for the solid solution $Ce_3Cu_xPt_{3-x}Sb_4$. The magnetic susceptibility varies from Ce^{3+} Curie-Weiss behavior in $Ce_3Cu_3Sb_4$ to almost Ce^{4+} behavior (intermediate valence) in $Ce_3Pt_3Sb_4$. All samples had semiconducting resistivities with decreasing activation energies for higher copper concentrations. The large positive thermopower of $Ce_3Pt_3Sb_4$ is greatly affected by small concentrations of copper. The peak of ~300 μV/K at approximately 110 K for $Ce_3Pt_3Sb_4$ changes to approximately -170 μV/K for $Ce_3Cu_{0.5}Pt_{2.5}Sb_4$ at the same temperature. For all the copper-doped samples, the thermopower changes from positive to negative values on cooling. [S0163-1829(99)14831-8]

I. INTRODUCTION

$Ce_3Pt_3Sb_4$ is a narrow gap *f*-electron system, often referred to as a Kondo insulator.[1] Magnetic susceptibility measurements have shown that the cerium is in a valence fluctuation or intermediate valence regime while the electrical resistivity displays activated semiconducting behavior.[2–5] Recently, we investigated the electrical resistivity ρ, thermopower S, and thermal conductivity κ of $Ce_3Pt_3Sb_4$ as a function of Nd doping on the Ce site.[6] One of the interesting observations of this work was that the temperature dependence of the electrical resistivity changed dramatically with neodymium doping.[6] The neodymium-doped samples did not show semiconducting behavior but instead had large broad peaks in the resistivities that resembled those of metallic cerium intermediate valence compounds (such as $CePd_3$).[7–10] The results also showed that the thermoelectric figure of merit $Z=S^2/\rho\kappa$ could be increased with neodymium doping. However, the maximum value of ZT (approximately 0.12 at $T=230$ K) was still far below those of good thermoelectric materials ($ZT\approx 1$). Continuing this work, we have started to investigate the effects of other chemical substitutions in $Ce_3Pt_3Sb_4$.

As previously reported, substituting various elements on the antimony site has proved difficult[6] and thus this paper explores doping on the platinum site. Both $Ce_3Au_3Sb_4$ (Ref. 2) and $Ce_3Cu_3Sb_4$ (Ref. 11) have been reported in the literature while attempts here to form other $Ce_3M_3Sb_4$ analogs (with $M=$ Ag, Pd, Ni, Co, and Fe) have been unsuccessful (see the experimental section). Although the thermopower of the $Ce_3Au_xPt_{3-x}Sb_4$ series has not been investigated, the magnetic and transport properties have already been well explored.[3–5] Thus, we focused on the magnetic and thermoelectric properties of the $Ce_3Cu_xPt_{3-x}Sb_4$ series.

$Ce_3Pt_3Sb_4$ has the complex, cubic, $Y_3Au_3Sb_4$ structure type[12] well described as a filled variation of the Th_3P_4 structure[13] (the platinum atoms occupy the vacancies in the Th_3P_4 structure). A polyhedral representation of the structure, depicted previously,[6] is useful in picturing this structure. However, this description does not necessarily describe the cerium coordination well. In particular, it should be noted that both the antimony and the platinum atoms are within a bonding distance of the cerium atoms. Thus, it is important to emphasize that substitution on the platinum site is likely to influence the intermediate valence nature of the cerium.

The first report of $Ce_3Cu_3Sb_4$ suggests that it does crystallize in the expected $Y_3Au_3Sb_4$ structure type [$a=9.721(1)$ Å] and displays a full Ce^{3+} moment ($\mu_{\rm eff}=2.59\mu_B$ and $\theta=10$ K).[11] It also reports an almost temperature-independent resistivity on an arc melted sample (~6.5 mΩ cm from 100–300 K) and a relatively large room temperature thermopower (~60 μV/K) that decreases linearly (and remains positive) with decreasing temperature.[11] A recent and more comprehensive report on the thermoelectric properties of $Ce_3Cu_3Sb_4$ obtained similar thermopower values.[14] The temperature dependence of the resistivity between 100 and 300 K also looks similar to the original report, except the over magnitude is lower (~2 mΩ cm).[14] Below 100 K the resistivity increases until peaking at 4 K (~8 mΩ cm). These measurements were made on a sintered pressed pellet and suggest, as in $Ce_3Au_3Sb_4$ (Refs. 3 and 15) and $Ce_3Pt_3Sb_4$ (Ref. 15), that the resistivities may be sample dependent. The report also gives a slightly larger lattice constant (9.765 Å) but similar magnetic moment ($\mu_{\rm eff}=2.50\mu_B$).[14]

Other previous reports suggest that $Ce_3Cu_3Sb_4$ adopts a tetragonally distorted variation of the $Y_3Au_3Sb_4$ structure type.[16,17] The evidence for this distortion appears to be only one split peak in the powder x-ray diffraction pattern that varies in intensity with batch and heat treatment.[16] Further analysis of $Ce_3Cu_3Sb_4$ presented here suggests that the peak in the powder x-ray diffraction pattern is more likely caused by a substantial amount of $CeCuSb_2$ impurity phase. $CeCuSb_2$ is a metallic phase that shows strong Kondo interactions and antiferromagnetic ordering at low temperatures.[18,19] Our attempts at synthesizing pure $Ce_3Cu_3Sb_4$ suggest that some $CeCuSb_2$ is invariably present. This may explain some of the variability in the reported properties of $Ce_3Cu_3Sb_4$.

Although pure $Ce_3Cu_3Sb_4$ may be difficult to synthesize, the phase certainly exists and should allow for the formation and study of the $Ce_3Cu_xPt_{3-x}Sb_4$ solid solution. The nature

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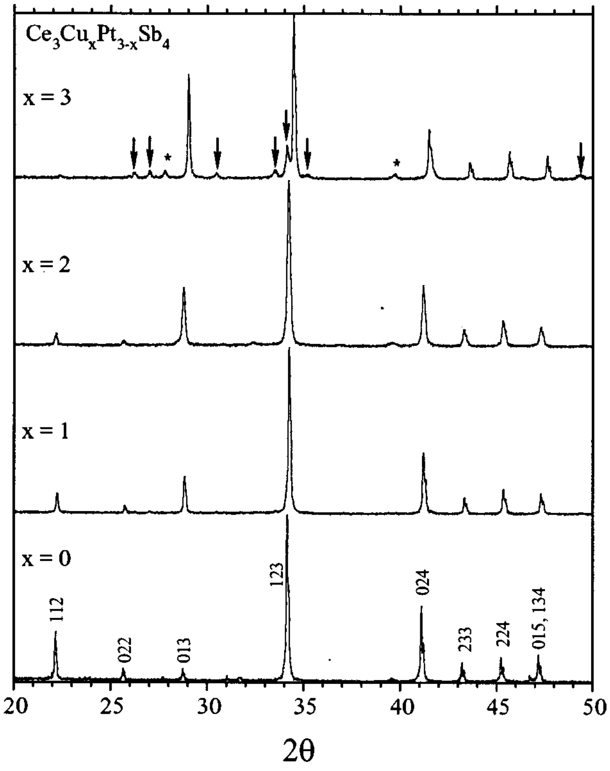


FIG. 1. The powder x-ray diffraction patterns Cu $K\alpha_1$ and $K\alpha_2$ radiation) for selected members of the $Ce_3Cu_xPt_{3-x}Sb_4$ series. The $Ce_3Cu_3Sb_4$ sample has a substantial $CeCuSb_2$ impurity (arrows) as well as a CeSb impurity (*). The Miller indexes are shown on the $Ce_3Pt_3Sb_4$ pattern.

of the cerium changing from intermediate valence behavior in $Ce_3Pt_3Sb_4$ to normal valence behavior in $Ce_3Cu_3Sb_4$ should have interesting effects on the properties of the compounds. Additionally, the fact that $Ce_3Cu_3Sb_4$ is reported to have a moderately large positive thermopower suggests that interesting thermoelectric behavior may be present across the whole series.

II. EXPERIMENT

The $Ce_3Cu_xPt_{3-x}Sb_4$ samples were synthesized using the arc melting and annealing procedures described previously.[6] The samples were shaped into rectangular bars (roughly $3 \times 3 \times 7\ mm^3$) by cutting with a diamond impregnated string saw. After cutting, the extra pieces of each sample were ground with a silicon standard (5.4301 Å), and analyzed by powder x-ray diffraction (Scintag θ-2θ diffractometer with Cu $K\alpha$ radiation). The x-ray diffraction patterns are shown in Fig. 1 (without the silicon) and the intensities agree well with simulated patterns.[20] The lattice constants obtained from a least-square fitting of the powder diffraction peak positions are shown in Fig. 2. The magnetic susceptibility data was collected at high fields (either 7500 G or 11 600 G) using a Quantum Designs MPMS SQUID magnetometer. The electrical resistivity and thermopower measurements were performed as described previously.[6] For low copper concentrations ($x<2$), indium could be used for electrical contacts. For higher copper concentrations ($x\geqslant 2$), silver epoxy was used to make the contacts.

As already mentioned, the $Ce_3Cu_3Sb_4$ sample could not be made single phase. Arc melting the elements to within 1% of the stoichiometric mass,[6] and annealing at 850 °C for 96 h, resulted in a sample with approximately 15% $CeCuSb_2$ (percentage based on peak heights in the powder x-ray diffraction pattern, see Fig. 1). Several attempts at making pure $Ce_3Cu_3Sb_4$ with both arc melting and pressed pellet syntheses were unsuccessful. Annealing conditions reported to work in the literature (600 °C for 3 weeks)[11,14] were also attempted for both synthetic methods. Unfortunately, these samples had even larger amounts of $CeCuSb_2$ impurity. Annealing the samples again at 850 °C or 1000 °C for 96 h did not improve the quality of the samples. Fortunately, the other $Ce_3Cu_xPt_{3-x}Sb_4$ compounds ($x\leqslant 2$) showed no signs of $CeCuSb_2$, and had only trace amounts of RESb and REPtSb second phases (<2% by peak height in the powder x-ray diffraction pattern).

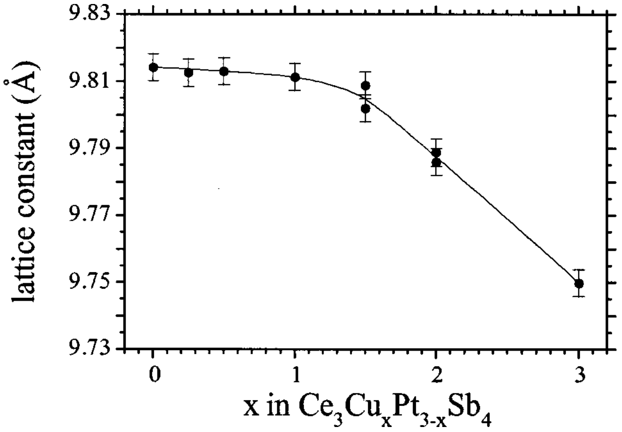


FIG. 2. Cubic lattice parameters for the $Ce_3Cu_xPt_{3-x}Sb_4$ series.

We also attempted to prepare $Ce_3M_3Sb_4$ analogs with $M=$ Fe, Co, Ni, Pd, and Ag. Analyzed by powder x-ray diffraction, all the samples were multiphase with CeSb being dominant in many of the samples ($M=$ Ni, Ag, Co, and Fe). Partial substitutions were also attempted: $Ce_3M_{0.5}Pt_{2.5}Sb_4$ with $M=$ Ag, Ni, and Co. In all cases, $Ce_3Pt_3Sb_4$ was the dominant phase but there were substantial impurity peaks suggesting that the M atoms were not alloying to a significant extent on the Pt site. A $Ce_3Rh_{0.3}Pt_{2.7}Sb_4$ sample yielded a multiphase compound with the predominant phase being CePtSb. The chemistry of the $Ce_3Pt_3Sb_4$ phase is very specific in that Cu and Au can alloy on the Pt site but Pd, Ag, and Ni will not.

III. RESULTS AND DISCUSSION

The lattice parameters for the $Ce_3Cu_xPt_{3-x}Sb_4$ series are shown in Fig. 2. The 9.814(4) Å value for $Ce_3Pt_3Sb_4$ agrees reasonably well with the reported value of 9.820 Å (Ref. 2). The value for $Ce_3Cu_3Sb_4$ [9.750(4) Å] in Fig. 2 is close to the values given in the literature: 9.721 Å (Ref. 11) and 9.765 Å (Ref. 14). However, since $Ce_3Cu_3Sb_4$ was not prepared as a single phase (see Fig. 1), there is the possibility that the stoichiometry is not well defined. This could influence the lattice parameters. It is important to note that the $Ce_3CuPt_2Sb_4$ sample does not have any $CeCuSb_2$ impurity and still has a reduced lattice constant in comparison to

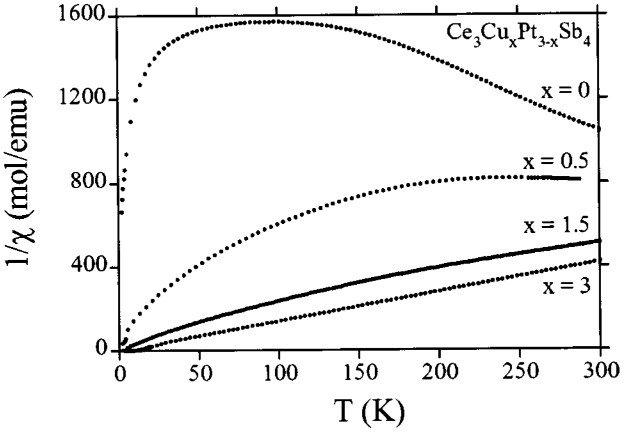


FIG. 3. The field cooled inverse magnetic susceptibility (collected at 7500 G or 11 600 G) as a function of temperature for selected members of the $Ce_3Cu_xPt_{3-x}Sb_4$ series.

$Ce_3Pt_3Sb_4$. Thus, the nonlinear behavior seen in Fig. 2 suggests that the intermediate valence nature of the cerium is changing throughout the $Ce_3Cu_xPt_{3-x}Sb_4$ series. This is what one might expect from the magnetic properties of the two end members: $Ce_3Pt_3Sb_4$ is intermediate valence and $Ce_3Cu_3Sb_4$ displays Curie Weiss Ce^{3+} behavior (described in detail later). However, this trend in lattice constants is unlike what has been reported for the $Ce_3Au_xPt_{3-x}Sb_4$ series where a reasonably linear variation was observed.[5] The 0.064(6) Å difference in lattice parameters between the two end members here is much smaller here than in the gold series (0.24 Å).[5]

The inverse magnetic susceptibilities of some of the compounds are shown as a function of temperature in Fig. 3. The susceptibility for $Ce_3Pt_3Sb_4$ agrees well with previous reports.[2,4] The data presented here shows a smaller low temperature Curie tail in comparison to the literature data, resulting in a slightly different peak shape of the $1/\chi$ plot. A minor amount of CePtSb impurity is the most likely cause for a paramagnetic Curie tail. $Ce_3Cu_3Sb_4$ shows Curie-Weiss behavior $[\mu_{\mathrm{eff}}=2.39(2)\mu_B$ and $\theta=1(1)\,\mathrm{K}]$ and agrees well with previous reports.[11,14,16,17] Ferromagnetic ordering at approximately 10 K has also been previously reported.[14,16,17] The critical temperature and nature of the magnetic ordering here is questionable because of the presence of substantial $CeCuSb_2$ impurities (the Curie-Weiss parameters are also not corrected for this impurity). Nevertheless, the low-temperature behavior is very similar to the previous report that suggested a tetragonal distortion in the structure.[17] For intermediate copper concentrations ($x=0.5$ and 1.5) the magnetic susceptibilities fall between those of the end members and do not follow simple Curie-Weiss behavior. There appears to be no magnetic ordering at low temperatures for these compounds (for $T>2$ K). Overall, the trends are similar to those for the $Ce_3Au_xPt_{3-x}Sb_4$ solid solution series.[5]

The resistivities of the $Ce_3Cu_xPt_{3-x}Sb_4$ samples are shown in Fig. 4. The resistivity for $Ce_3Pt_3Sb_4$ is slightly smaller in magnitude than for our previously reported sample, but the temperature dependence is very similar.[6] The magnitude of the resistivities are likely to be sample dependent for a variety of reasons. First, since these compounds are semiconducting there is a possibility that the values could be greatly affected by a small deviation from stoichiometry or small concentrations of impurities or defects. Because of the synthetic methods, the antimony concentration is not precisely controlled. The presence of a few percent of second phase, such as the metallic phase REPtSb (Ref. 21), might also contribute to differences. Upon further examination of the arc-melted samples it was also observed that small internal voids were occasionally present, presumably created by the sublimation of antimony during the arc-melting process. These voids would cause the calculated resistivities to be too high.

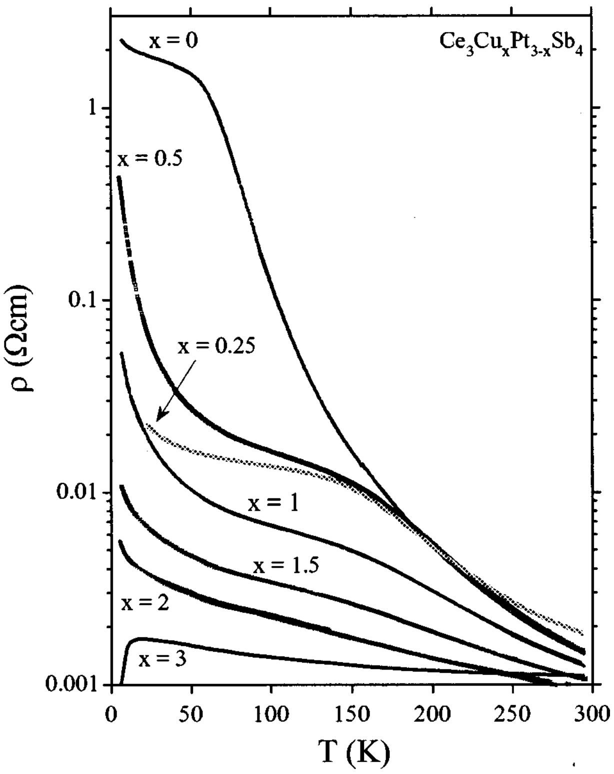
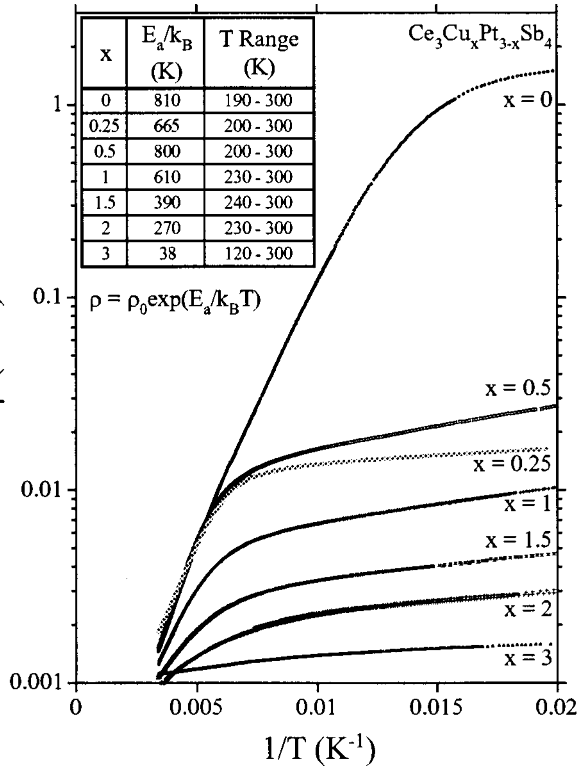


FIG. 4. The electrical resistivities (on a log scale) as a function of temperature for the $Ce_3Cu_xPt_{3-x}Sb_4$ compounds. The anomalous behavior of the $x=0.25$ sample (gray line) is discussed in the text.

As shown in Fig. 4, the resistivities tend to decrease with the addition of copper. Unlike the neodymium-doped samples,[6] the resistivities remain semiconducting at all copper concentrations. This is similar to the behavior of the $Ce_3Au_xPt_{3-x}Sb_4$ solid solution series.[5] For interest, one neodymium-doped sample of $Ce_3CuPt_2Sb_4$ was prepared. Only 5% of the Ce was replaced by Nd to see if small amounts of Nd could have the same dramatic effect on the resistivity as with the pure $Ce_3Pt_3Sb_4$ compound (i.e., would the resistivity look like that of an intermediate valence metal). Interestingly, the resistivity of $Nd_{0.15}Ce_{2.85}CuPt_2Sb_4$ maintained a semiconducting temperature dependence and was nearly identical to that of $Ce_3CuPt_2Sb_4$.

The resistivities of the $Ce_3Cu_xPt_{3-x}Sb_4$ samples plotted as a function of $1/T$ (Fig. 5) clearly show that the band gap of $Ce_3Pt_3Sb_4$ decreases with increasing concentrations of copper. The high-temperature resistivity data can be fit to an activation law $\rho=\rho_0\exp(E_a/k_BT)$, and the activation energies are listed in Fig. 5 (to an estimated 5% error). The fit for $Ce_3Pt_3Sb_4$ agrees well with our previous report over the 190



x	E_a/k_B (K)	T Range (K)
0	810	190 - 300
0.25	665	200 - 300
0.5	800	200 - 300
1	610	230 - 300
1.5	390	240 - 300
2	270	230 - 300
3	38	120 - 300

FIG. 5. The $Ce_3Cu_xPt_{3-x}Sb_4$ electrical resistivities (on a log scale) as a function of $1/T$. The high temperature data agrees well with the fit: $\rho = \rho_0 \exp(E_a/k_BT)$. The anomalous behavior of the $x = 0.25$ sample (gray line) is discussed in the text.

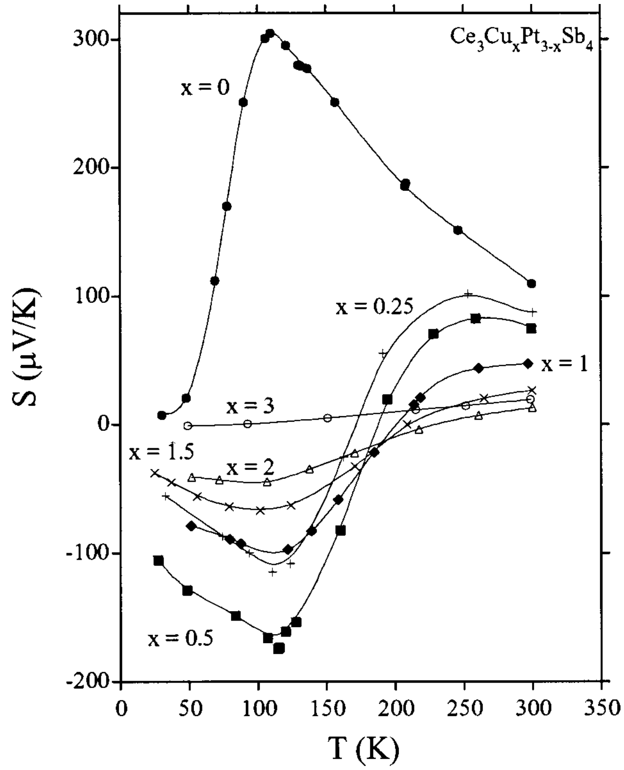


FIG. 6. The thermopower as a function of temperature for the $Ce_3Cu_xPt_{3-x}Sb_4$ compounds.

to 300 K temperature range.[6] Fitting to lower temperatures (i.e., 100–300 K) shifts the derived E_a/k_B value somewhat lower.[6] The values in the literature range from approximately 500[2,3,5] to 760 K.[15] At higher concentrations of copper, the interpretation of the derived E_a/k_B value is questionable because $E_a \approx k_BT$ and the range over which the linear region extends is small. The fit for $Ce_3Cu_3Sb_4$ is also highly questionable because of the $CeCuSb_2$ impurity. However, it is interesting to note that the literature report suggesting the tetragonal distortion in $Ce_3Cu_3Sb_4$ also reports an activation energy of 40 K.[16] Overall, it does appear that with increasing copper concentration the gap decreases, becoming almost semimetallic at $x = 3$. Recently, a zero-gap semiconductor model has been proposed to explain the properties of the isoelectronic $Ce_3Au_3Sb_4$.[15]

In both Figs. 4 and 5, the data for $Ce_3Cu_{0.25}Pt_{2.75}Sb_4$ does not fit with the apparent smooth evolution of properties seen in the other samples. When cut in half, the arc-melted bar used in the resistivity had a large number of internal voids. Further powder x-ray characterization of that sample also revealed larger amounts of CePtSb impurity than originally determined (up to 15% based on peak heights). This probably explains the anomalous low temperature resistivity of that sample. The activation energy (E_a/k_B) is also low but reasonable considering the ±5% error.

The thermopowers of the $Ce_3Cu_xPt_{3-x}Sb_4$ compounds are shown in Fig. 6. The values for $Ce_3Pt_3Sb_4$ agree well with our previous report: the peak is slightly lower in magnitude, probably resulting from different concentrations of impurities within the samples.[6] The rapid decrease in thermopower at lower temperatures (for the $x = 0$ sample) has been investigated more thoroughly here and suggests that $S > 0$ for $T < 300$ K. The other end member, $Ce_3Cu_3Sb_4$, has a thermopower that is roughly linear with temperature reaching 20 μV/K by 300 K. This is lower than previous reports of approximately 60 μV/K (Ref. 11, 14); however, the metallic $CeCuSb_2$ impurity present in this sample will likely lower the thermopower values.

As seen from Fig. 6, small concentrations of copper in $Ce_3Pt_3Sb_4$ certainly make large differences to the thermopower. With 16% Cu on the Pt site ($x = 0.5$), the $Ce_3Pt_3Sb_4$ thermopower peak changes from approximately +300 μV/K to a minima of −170 μV/K. Interestingly, the feature remains near the same temperature (~110 K), a characteristic common for all the copper-doped samples. The significance of this temperature is not yet clear. It may reflect a characteristic energy for the interaction between the $4f$ electrons and the conduction electrons. It is surprising that this interaction does not change since the lattice constant, and presumably the Kondo temperature, are changing with the chemical substitution.

The change from positive to negative thermopowers in these copper-doped $Ce_3Pt_3Sb_4$ samples suggests the presence of both carrier types. The large changes in magnitude also suggest that the holes and electrons may have considerably different mobilities. Both end members have positive thermopowers and thus would seem to be dominated by holes. Hall effect measurements on these compounds would be interesting and may help explain the significance of the 110 K peak temperature. However, if two carrier types are indeed present this data may be difficult to interpret. The semiconducting properties of these compounds make comparisons to other cerium intermetallics difficult. There are other cerium-based intermetallics that show thermopower sign changes as a function of temperature;[22] however, these features are often related to antiferromagnetic ordering or other features in the transport properties that are not apparent here. In addition, the thermopower values here are roughly an order of magnitude larger than in these other compounds.[22]

Overall, the changes in sign upon cooling result in the thermopower becoming zero at some intermediate temperature. This precludes these compounds from being considered as useful thermoelectric materials over a large temperature region below 300 K.[6] Additionally, the semiconducting resistivities that increase exponentially as the temperature is lowered, also prevent these materials from having a high *ZT*. It is interesting to speculate what would happen if a transition metal with one less electron than platinum could be substituted into $Ce_3Pt_3Sb_4$. Here with copper (one extra electron), the thermopower values are driven substantially negative. Could the thermopowers be driven even more positive than $Ce_3Pt_3Sb_4$ with a transition metal having fewer electrons? Unfortunately, both Co and Rh do not alloy on the Pt site.

IV. CONCLUSIONS

The solid solution between the semiconducting Kondo insulator $Ce_3Pt_3Sb_4$ and the normal valence $Ce_3Cu_3Sb_4$ were studied. The magnetic susceptibility displayed the expected trends for intermediate concentrations of copper. All samples had semiconducting resistivities with decreasing activation energies for higher Cu concentrations. These magnetic and electrical properties are very similar to the $Ce_3Au_xPt_{3-x}Sb_4$ solid solution series previously reported.[5] Unfortunately, the thermoelectric properties of that series were not studied. Here, the large positive thermopower of $Ce_3Pt_3Sb_4$ is greatly affected by small concentrations of copper. The peak of $\sim 300\ \mu$V/K at approximately 110 K for $Ce_3Pt_3Sb_4$ changes to about $-170\ \mu$V/K for $Ce_3Cu_{0.5}Pt_{2.5}Sb_4$ at the same temperature. For all the copper-doped samples, the thermopower changes from positive to negative values on cooling. This suggests that these compounds are unlikely to be useful thermoelectric materials since at some intermediate temperature the thermopower is zero.

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