PHYSICAL REVIEW B, VOLUME 64, 121104

Suppression of the resistivity anomaly and corresponding thermopower behavior in the pentatelluride system by the addition of Sb: $Hf_{1-X}Zr_XTe_{5-Y}Sb_Y$

R. T. Littleton IV,[1] Terry M. Tritt,[1] J. W. Kolis,[2] D. R. Ketchum,[2] Nathan D. Lowhorn,[1] and M. B. Korzenski[2]
[1]*Department of Physics and Astronomy, Clemson University, Clemson, South Carolina 29634*
[2]*Department of Chemistry, Clemson University, Clemson, South Carolina 29634*

(Received 30 January 2001; published 10 September 2001)

The electrical resistivity ρ and the thermopower α of the transition-metal pentatelluride system $Hf_{1-X}Zr_XTe_{5-Y}Sb_Y$ have been measured over a broad range of temperature, $10\,K < T < 300\,K$. The systematic Sb doping of these materials has been performed over a range from $0 < Y < 0.75$, where Y is the nominal Sb concentration. Both parent materials ($HfTe_5$ and $ZrTe_5$) exhibit an anomalous resistive peak, $T_P \approx 80\,K$ for $HfTe_5$ and $T_P \approx 145\,K$ for $ZrTe_5$. Each parent material displays a large positive (p-type) thermopower ($\alpha \geqslant +125\,\mu V/K$) around room temperature, which undergoes a change to a large negative (n-type) thermopower ($\alpha \leqslant -125\,\mu V/K$) below the peak temperature. At a specific level of Sb doping the resistive anomaly is no longer evident and results in a semimetallic temperature dependence. In addition the thermopower monotonically decreases with temperature with no change in sign as in the parent materials. X-ray-diffraction data reveals that the pentatelluride structure is still preserved at all doping concentrations.

DOI: 10.1103/PhysRevB.64.121104 PACS number(s): 61.10.Nz, 72.15.−v, 73.50.Lw

INTRODUCTION

Recently, we have been investigating a class of quasi-one-dimensional materials known as transition-metal pentatellurides, with parent compositions of $HfTe_5$ and $ZrTe_5$.[1,2] Both $HfTe_5$ and $ZrTe_5$ exhibit a resistive anomaly peak, $T_P \approx 80\,K$ for $HfTe_5$ and $T_P \approx 145\,K$ for $ZrTe_5$ as shown in the inset of Fig. 1. The magnitude of this resistive anomaly is typically 3–7 times the room temperature value of $\rho < 1\,m\Omega\,cm$. As shown in the inset of Fig. 2, each of the parent materials displays a large positive (p-type) thermopower ($\alpha \geqslant +125\,\mu V/K$) around room temperature that undergoes a change to a large negative (n-type) thermopower ($\alpha \geqslant -125\,\mu V/K$) below the peak temperature. The zero crossing of thermopower T_0 correlates very well with the peak in the resistivity T_P. Because of the relatively high magnitude of the thermopower and favorable electrical resistivity values at and below room temperature, these materials have shown promise as potential low-temperature thermoelectric materials.[3]

Over the past six to seven years, there have been increased efforts in investigating new materials as the next generation thermoelectric materials[4–6] especially for low-temperature applications.[7] The potential of a material for use as a thermoelectric is determined by a dimensionless figure of merit, $ZT = \alpha^2 \sigma T/\lambda$, where α is the Seebeck coefficient, σ is the electrical conductivity, and λ is the thermal conductivity. The numerator or power factor $\alpha^2 \sigma T$ can typically be tuned through chemical doping and substitution. An ideal thermoelectric material will exhibit high phonon scattering and low electron scattering. Low-temperature thermoelectric materials are even more difficult to achieve, since the absolute value of the thermopower typically decreases with decreasing temperature.

In metals, the thermopower is typically proportional to temperature, i.e., Mott diffusion thermopower.[8]

$$\alpha \approx \frac{\pi^2 k_B^2 T}{3e} \left. \frac{\partial \ln \sigma(E)}{\partial E} \right|_{E_F}.$$

Semiconducting materials exhibit a thermopower that is proportional to $1/T$ (as well as a temperature-activated conductivity). One of the important issues relative to low-temperature thermoelectric materials is utilizing possible mechanisms, which may produce high thermopower at low temperatures. A number of systems that are candidates for low-temperature thermoelectric materials are heavy fermion materials, Kondo systems and quasi-one-dimensional materials. Low dimensional systems are known to be susceptible to van Hove singularities (or cusps) in their density of states $g(E)$ electronic phase transitions, and exotic transport properties, which can add structure in $g(E)$ near E_F. Doping can produce substantial effects in these types of materials and can drastically change their electronic transport.

Previously, we performed doping investigations on both the Hf or Zr metal site (using, Hf, Zr, Ti, Nb, Ta, etc.) and the Te site, primarily with Se.[3] These materials easily allow

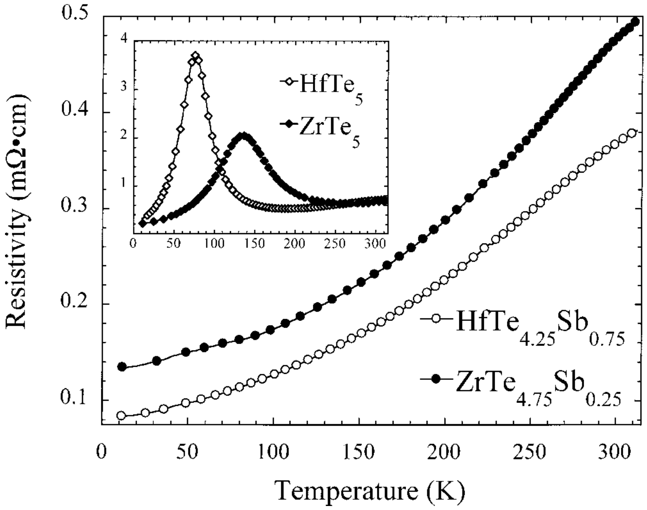

FIG. 1. A plot of the resistivity as a function of temperature for the Sb-doped pentatellurides at the levels as indicated in the figure. (Inset: A plot of the resistivity as a function of temperature for the parent pentatellurides, $HfTe_5$ and $ZrTe_5$ as indicated in the inset.)

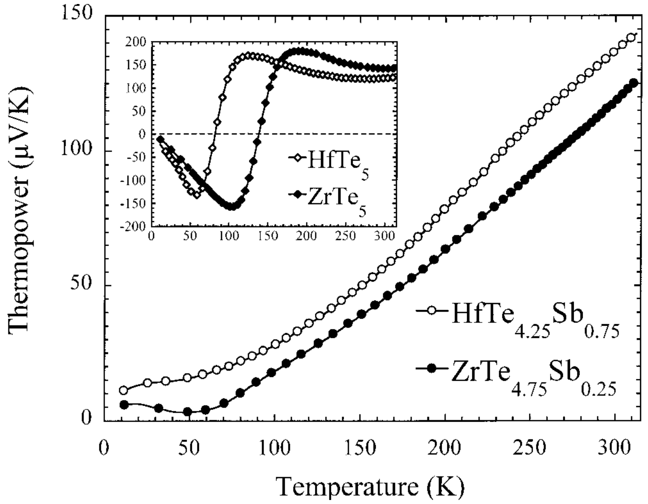

FIG. 2. A plot of the thermopower as a function of temperature for the Sb-doped pentatellurides at the levels as indicated in the figure. (Inset: A plot of the thermopower as a function of temperature for the parent pentatellurides, $HfTe_5$ and $ZrTe_5$ as indicated.)

compositional substitutions and form solid solutions between Hf and Zr ($Hf_{1-X}Zr_XTe_5$) for $x=0$ to $x=1$. The resistivity anomaly and corresponding thermopower or T_P and T_0 systematically shift with temperature from $T_P=80\,\mathrm{K}$ for $x=0$ (i.e., parent $HfTe_5$) to $T_P=145\,\mathrm{K}$ for $x=1$ (i.e., parent $HfTe_5$). The addition of Ti to the system shifts both T_P and T_0 to lower temperature for both parent systems.[2] The addition of Se to the system, presumably substituting for the Te atoms, yields an enhancement of the thermopower and corresponding decrease in the resistivity for both parent systems. The Se system ($Hf_{1-X}Zr_XTe_{5-Y}Se_Y$) yields thermoelectric behavior that is more favorable than current state of the art thermoelectric materials. In this paper we report the effect of Sb substitution ($Hf_{1-X}Zr_XTe_{5-Y}Sb_Y$), and the resulting effect on the electrical transport properties, as a function of temperature is presented between 10 and 300 K.

EXPERIMENTAL PROCEDURE

Single crystals of both the pure and doped materials were grown in conditions similar to previously reported methods.[9] A stoichiometric ratio of the elements were sealed in a fused silica tube with iodine (≈5 mg/mL) and placed in a tube furnace. Reactants were placed at the center of the furnace while the other end of the reaction vessel is placed near the cooler end of the furnace to provide a temperature gradient. Crystals of the materials were obtained in excess of 1.5 mm long and 100 μm in diameter with the preferred direction of growth along the a axis, as determined by face indexing. These are long chain systems with an orthorhombic crystal structure.[10] They exhibit slightly anisotropic transport properties with the high conductivity axis along the growth axis (a axis). Electrical contact was made using Au wires bonded to the crystal with Au paint. The electrical resistivity and thermopower of each sample was measured in a closed-cycle refrigerator from approximately 10 to 300 K. The resistance of the sample was measured using a standard four-probe technique and the thermopower was measured simultaneously. Details of experimental procedure are discussed elsewhere.[11] The x-ray-diffraction data was obtained on an Rigaku AFC 7 single-crystal diffractomer equipped with a Mercury CCD detector. Data were obtained on suitable high-quality single crystals of both doped and undoped samples at room temperature and 140 K. Unit-cell data confirmed unequivocally that the structure is unchanged upon doping.

Due to the small size of these samples the thermal conductivity is very difficult to determine. We have recently developed an apparatus using a technique called the parallel thermal conductance method to measure the thermal conductivity for such needlelike samples.[12] Results on the thermal conductivity of the parent pentatelluride materials are presented elsewhere[13] and measurements of the Sb-doped pentatellurides are in progress.

In all the doping or substitution cases discussed previously, the signature behavior of the pentatelluride system (the resistive anomaly and corresponding thermopower behavior) observed in the parent materials is maintained in these doped systems. In this paper, a systematic investigation of the effect of Sb doping (from $0<Y<0.75$) on the thermoelectric properties of $Hf_{1-X}Zr_XTe_{5-Y}Sb_Y$, is presented. Microprobe measurements appear to confirm that the initial presumption that Sb substitutes for the Te, however, the exact concentrations are difficult to ascertain, as will be discussed later in the paper. The concentrations indicated in this paper are nominal concentrations. The resistivity and thermopower are shown in Figs. 1 and 2 as function of temperature for the highest level of Sb doping, with a nominal concentration of Sb substitution for Te for the Sb-doped $HfTe_{5-Y}Sb_Y$ ($Y=0.75$) and $ZrTe_{5-Y}Sb_Y$ ($Y=0.25$).

At a certain level in the Sb-doped pentatellurides ($Hf_{1-X}Zr_XTe_{5-Y}Sb_Y$), the addition of Sb, presumably for Te totally suppresses the resistive anomaly and both the resistivity and the thermopower decrease monotonically with decreasing temperature in a "metallic" or "semi-metallic" manner. As seen in Fig. 1, the temperature derivative of the resistivity for both $HfTe_{5-Y}Sb_Y$ and $ZrTe_{5-Y}Sb_Y$ is positive, $dR/dT>0$, over the whole temperature range measured, $10\,\mathrm{K}\leqslant T\leqslant 300\,\mathrm{K}$. The temperature dependence is in strong contrast with that of the parent materials as shown in the inset of Fig. 1, however, the room-temperature magnitudes are comparable. In addition, the thermopower for both $HfTe_{5-Y}Sb_Y$ and $ZrTe_{5-Y}Sb_Y$, shown in Fig. 2, maintains the relatively high values ($\alpha>120\,\mu\mathrm{V/K}$ at 300 K) that are evident in the parent materials. However the thermopower of the Sb-doped pentatellurides decreases monotonically with decreasing temperature, which is in strong contrast to the parent materials as shown in the inset in Fig. 2.

The resistivity and thermopower for lower levels of Sb doping (nominal concentration from $0<Y<0.05$) for the pentatelluride system ($ZrTe_{5-Y}Sb_Y$) is shown as a function of temperature in Figs. 3(a) and 3(b), respectively. As evident from this figure, low levels of Sb doping make the data very difficult to interpret. The shifts in temperature of T_0 and T_P are not systematic, as was the case for substitutions of Hf and Zr on the metal site ($Hf_{1-X}Zr_XTe_5$).[14] We have performed extensive electron microprobe analysis on these samples and

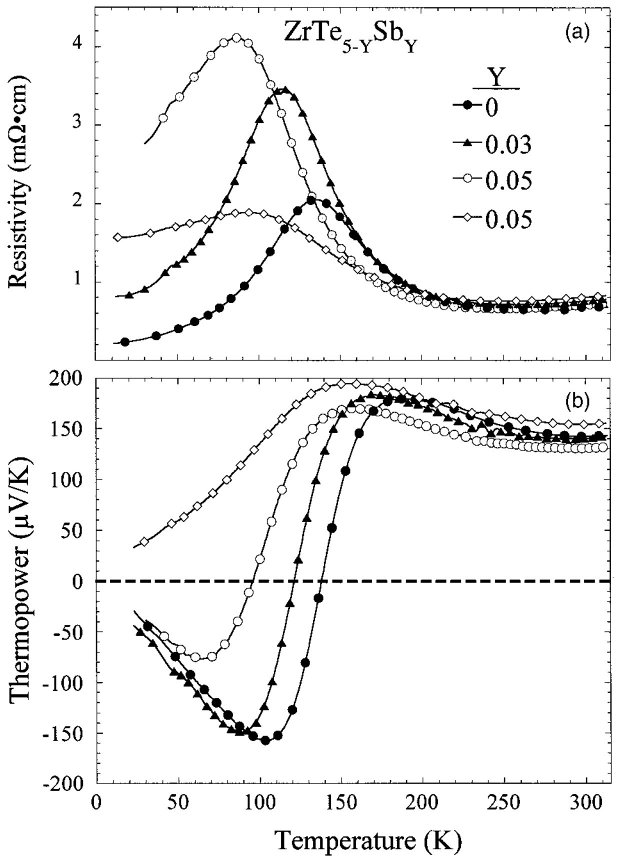

FIG. 3. A plot of the resistivity (a) and thermopower (b) as a function of temperature for the Sb-doped pentatellurides for various levels of Sb as indicated in the figure. These levels as indicated in the figure are the nominal concentrations of the elemental concentrations of the mixed powders.

the data is somewhat inconclusive. We found it very difficult to detect these low levels of Sb doping. We have included data on the parent material ($ZrTe_5$) for comparison. From Fig. 3, only for the sample represented by open diamonds is the Sb concentration high enough to exceed the microprobe detection limit. Unfortunately, many of the low levels of Sb doping were very near the detection limit of the apparatus. For the parent compound $ZrTe_5$ (solid circles) and the small nominal concentrations, obviously only small amounts of Sb are present in the crystal, however, the effects are very apparent in the transport properties shown in Figs. 3(a) and 3(b). When the level of Sb reaches $Y \approx 0.05$, there is a distinct change in the resistivity and thermopower. The resistivity still shows a small peak, but is relatively temperature independent below the peak. The thermopower does not change sign to the high negative values, but decreases monotonically below the peak with decreasing temperature. We have found that when $Y \geqslant 0.2$ that the peak in the resistivity is suppressed. However, we found that the determination of the Sb concentration for $Y \geqslant 0.2$ was somewhat inconclusive, since the amounts were inconsistent along the length of the sample.

The first question that must be answered is whether or not this material is still a pentatelluride single crystal or has a structural change occurred with the Sb substitution. Thus, we performed single-crystal x-ray diffraction on samples of both the parent and Sb-doped crystals. Indeed, analysis of the single-crystal x-ray-diffraction data on the parent compounds and the Sb-doped needlelike crystals, confirmed that each exhibit the pentatelluride structures, as shown in Table I. This data confirms that both parent and the Sb-doped crystals ($ZrTe_5$ and $ZrSb_{0.5}Te_{4.5}$, as well as $HfTe_5$ and $HfSb_{0.1}Te_{4.9}$) are consistent with an orthorhombic space group $C222$ or *Cmcm* designation. The lattice parameters at $T \approx 300$ K and $T = 150$ K are consistent between the parent systems and the doped systems within experimental uncertainty of the experimental data.

Thus, the drastic change in the electrical transport properties is not a result of some type of structural change. Previous studies that we have performed have also shown great sensitivity to other types of doping both on the transition-metal site as well as the chalcogenide site but without a suppression of the resistive anomaly. Accurate Hall measurements are difficult on samples of this size and we have not yet determined the carrier concentration. However, the Sb substitution completely suppresses the resistive anomaly and it would be unlikely this is just due to a change in carrier concentration. We presume that the dramatic changes are due to the substitution of Sb $(5p^3)$ for Te $(5p^4)$, which results in a pronounced affect on the low-temperature electrical trans-

TABLE I. Single crystal x-ray diffraction data for $Hf_{1-X}Zr_XTc_{5-Y}Sb_Y$ in orthorhombic space group C_{222} or M_{MCM}.

	Temp. (K)	$ZrTe_5$	$ZrSb_{0.5}Te_{4.5}$	$HfTe_5$	$HfSb_{0.1}Te_{4.4}$
a(Å)	298	3.8(6)	3.9(2)	3.91(5)	3.9(8)
b(Å)	298	14.4(7)	14.4(9)	14.8(0)	14.5(3)
c(Å)	298	13.8(1)	13.9(9)	13.8(8)	13.7(1)
V(Å)	298	711.155	765.872	774.58	776.694
$\alpha=\beta=\gamma$	298	90.0	90.0	90.0	90.0
a(Å)	150	3.7(8)	3.9(2)	3.93(4)	3.99(9)
b(Å)	150	15.0(4)	14.0(7)	14.6(8)	14.5(2)
c(Å)	150	14.1(2)	13.7(7)	13.8(9)	13.7(4)
V(Å^3)	150	736.933	770.251	756.278	777.508
$\alpha=\beta=\gamma$	150	90.0	90.0	90.0	90.0

port in this system. This would seem to indicate that the anomalous electronic behavior in the parent materials originates or is dominated by the overlap of the *p* orbitals associated with the Te bonds. Through investigation of the low-temperature Shubnikov–de Haas (S-dH) effect, Kamm *et al.* found that there are two electron bands and one hole type band in the parent materials.[15] They found a very anisotropic Fermi surface with very different effective masses in the two transverse directions. It was previously postulated that the electronic transport behavior at or near room temperature appears to be dominated by a high mobility hole band.[1,14] It appears that the hole band becomes ‘‘gapped’’ as the temperature is reduced and the transport transforms to an electron dominated conduction. From the current data on the Sb-doped systems as shown in Figs. 1 and 2, it appears that the high mobility *p*-type band dominates the electrical conduction over the entire temperature range investigated. It would be very interesting to perform S-dH measurements on the Sb-doped pentatellurides.

The data on the Sb doping, which is shown in Figs. 1 and 2, is very important to the potential of these materials for possible low-temperature thermoelectric materials. High values of *p*-type thermopower ($\alpha \approx 120\,\mu\mathrm{V\,K}$) have been maintained, while the room-temperature resistivity for this Sb-doped material is somewhat lower ($\rho \approx 0.5\,\mathrm{m}\Omega$ cm) than the parent materials. In the parent materials, as well as other previous substitutions, the presence of the anomaly reduces the potential performance of these materials due to the increased resistivity at lower temperatures. In the higher concentration Sb-doped material, the resistivity and the thermopower declines with decreasing temperature over the entire temperature range studied with a possible small phonon-drag contribution below 40 K. The power factor ($\alpha^2\sigma T$) for the higher concentration Sb-doped materials compare very well with those of the state of the art $\mathrm{Bi_2Te_3}$ with values of 1.6 and 0.9 W/(m K) for $\mathrm{HfTe}_{5-Y}\mathrm{Sb}_Y$ and $\mathrm{ZrTe}_{5-Y}\mathrm{Sb}_Y$, respectively at room temperature. Preliminary measurements of the thermal conductivity of the parent compounds have shown that the thermal conductivity is around 4–8 W/m K around room temperature.[13] One would not expect large changes in the lattice thermal conductivity values, given the level of Sb doping indicated in this study. The results from the Sb doping makes these materials very interesting for future work, especially in relation to their potential development as low-temperature thermoelectric materials.

SUMMARY

We have investigated the effect of Sb doping on the thermoelectric properties of the transition-metal pentatellurides, $\mathrm{Hf}_{1-X}\mathrm{Zr}_X\mathrm{Te}_{5-Y}\mathrm{Sb}_Y$. Small levels of Sb doping, $Y \geqslant 0.05$, alters the resistive anomaly and affects the temperature dependence of the thermopower. Unfortunately, it is very difficult to detect the exact amount of Sb in the crystals for these small percentages since we are close to the detection limit of the instrument. At the higher concentrations of Sb on the order of $Y \approx 0.2$, dramatic effects are seen in the electrical transport. The resistive anomaly is totally suppressed. The thermopower values remain relatively high and *p*-type, $\alpha \approx 120\,\mu\mathrm{V/K}$ while the resistivity is somewhat lower than the parent materials. Both the resistivity and the thermopower decrease monotonically from room temperature with decreasing temperature in a semimetallic manner. These values yield a power factor that is comparable to that of the state-of-the-art $\mathrm{Bi_2Te_3}$ thermoelectric materials.

Future work will include more extensive doping of Sb and other elements in attempts to further elucidate the origin of the resistivity anomaly in the pentatellurides. This is especially important to understand the differences between the parent materials and the Sb-doped materials, especially given that resistive anomaly is totally suppressed at a certain Sb level. Perhaps, S-dH and Hall measurements which we plan to perform may be able to yield important information about the differences in these materials. In addition it is hoped that these doping studies may be able to enhance the power factor of these materials for thermoelectric applications.

ACKNOWLEDGMENTS

We acknowledge support from the following grants: ONR No. N00014-98-1-0271, DARPA/ARO No. DAAG55-97-1-0267 and the SC Commission on Higher Education. We also acknowledge James J. McGee at the University of South Carolina for electron microprobe analysis.

---

[1] R. T. Littleton IV *et al.*, *Thermoelectric Materials, 1998*, edited by T. M. Tritt *et al.*, Mater. Res. Soc. Symp. Proc. No. 545 (Materials Research Society, Pittsburgh, 1998), pp. 381–396.

[2] R. T. Littleton IV *et al.*, Appl. Phys. Lett. **72**, 2056 (1998).

[3] R. T. Littleton IV, Terry M. Tritt, D. R. Ketchum, and J. Kolis, Phys. Rev. B **60**, 13 453 (1999).

[4] *Thermoelectric Materials 1997. New Directions and Approaches*, edited by T. M. Tritt *et al.*, Mater. Res. Soc. Symp. Proc. No. **478** (Materials Research Society, Warrenton, PA, 1997).

[5] See full proceedings in Ref. 1.

[6] Terry M. Tritt, Science **283**, 804 (1999).

[7] Duck-Young Chung *et al.*, Science **287**, 1024 (2000).

[8] R. D. Barnard, *Thermoelectricity in Metals and Alloys* (Taylor and Francis, London, 1972), p. 114.

[9] F. Levy and H. Berger, J. Cryst. Growth **61**, 61 (1983).

[10] S. Furuseth *et al.*, Acta Chem. Scand. **27**, 2367 (1973).

[11] A. L. Pope *et al.*, Rev. Sci. Instrum. (to be published).

[12] B. Zawilski *et al.*, Rev. Sci. Instrum. **72**, 1770 (2001).

[13] B. Zawilski, R. T. Littleton IV, and Terry T. Tritt, Appl. Phys. Lett. **77**, 2319 (2000).

[14] R. T. Littleton IV and Terry M. Tritt, *Thermoelectric Properties of the Transition Metal Pentatellurides*, Vol. 70 of Semiconductors and Semimetals, edited by Terry M. Tritt (Academic, New York, 2000).

[15] G. N. Kamm *et al.*, Phys. Rev. B **35**, 1223 (1987).