Large enhancement of the resistive anomaly in the pentatelluride materials $HfTe_5$ and $ZrTe_5$ with applied magnetic field

Terry M. Tritt*
Department of Physics and Astronomy and Materials Science and Engineering Department, Clemson University, Clemson, South Carolina 29634

Nathan D. Lowhorn
Department of Physics and Astronomy, Clemson University, Clemson, South Carolina 29634

R. T. Littleton IV
Materials Science and Engineering Department, Clemson University, Clemson, South Carolina 29634

Amy Pope
Department of Physics and Astronomy, Clemson University, Clemson, South Carolina 29634

C. R. Feger and J. W. Kolis
Department of Chemistry, Clemson University, Clemson, South Carolina 29634
(Received 10 March 1999)

The resistivity of single-crystal pentatellurides, $HfTe_5$ and $ZrTe_5$, has been measured as a function of temperature and applied magnetic field. At zero magnetic field these materials exhibit a peak in their resistivity (at T_P) as a function of temperature that corresponds to an, as yet, undetermined phase transition. The application of a transverse magnetic field ($B \perp$ to the current I) has a profound effect on the resistive peak in these materials, shifting the peak to slightly higher temperatures and producing a large enhancement of the resistivity at the peak, up to a factor of 3 in $ZrTe_5$ ($T_P = 145$ K) and 10 in $HfTe_5$ ($T_P = 80$ K). Larger magnetoresistance is observed at even lower temperatures, $T < 20$ K. [S0163-1829(99)06035-X]

INTRODUCTION

The low-dimensional pentatelluride materials, $HfTe_5$ and $ZrTe_5$, first synthesized in 1973,[1] exhibit a peak in their resistivity as a function of temperature, $T_P \approx 80$ K for $HfTe_5$ and $T_P \approx 145$ K for $ZrTe_5$, apparently the result of a phase transition.[2,3] In addition, both parent materials exhibit a large positive (p-type) thermopower ($\alpha \approx 150\ \mu$V/K) near room temperature which undergoes a change to negative thermopower (n-type, $\alpha \approx -150\ \mu$V/K) below the peak temperature with the zero crossing of thermopower T_0, corresponding well with T_P.[4] Early theories suggested that this resistive anomaly was probably due to a charge-density wave (CDW) transition, similar to that which occurs in $NbSe_3$.[5] However, the absence of distinct superlattice spots in the x-ray diffraction patterns and the absence of nonlinear conductance, both indicative of CDW materials, seemed to quickly contradict this explanation.[6] Other experiments were attempted in an effort to ascertain the nature and origin of this yet undetermined transition. Magnetic susceptibility measurements failed to elucidate any magnetic character to the observed transition in these pentatellurides, i.e., there was no structure of features near the peak. These materials are diamagnetic and show a small paramagnetic character at low temperatures attributed to impurities.[5] Fermi-surface determinations by Kamm *et al.* revealed a very anisotropic Fermi surface for these materials, with an ellipsoidal shape and an effective mass which was quite different in the two directions. The effective mass along the b axis was calculated to 100 times greater than that along the a axis.[7,8] Pressure effects and the effect of an applied stress indicated substantial changes in the magnitude of the resistive peak (and thermopower) or the corresponding peak temperature.[9] The room-temperature resistivity of the materials are 0.71 mΩ cm for $HfTe_5$ and 0.67 mΩ cm for $ZrTe_5$, indicating a semimetallic nature.

We are currently studying these materials in relation to their potential for thermoelectric refrigeration applications at low temperatures.[10,11] This potential is primarily due to the relatively large thermopower, $\alpha \approx \pm 150\ \mu$V/K, that is observed in these materials at low temperatures, which leads to a large Peltier effect. We have performed careful doping studies of these materials and have been able to form solid solutions of these materials, $Hf_{1-x}Zr_xTe_5$ (where $x = 0$ to 1) and $M_{1-x}Y_xTe_5$ (where M = Hf, Zr, and Y = Ti, Ta, and Nb) at concentrations of $x \leqslant 10\%$. In the $Hf_{1-x}Zr_xTe_5$ materials, T_P and T_0 systematically shift from approximately $T = 80$ K for $x = 0$ to $T = 145$ K for $x = 1$. The addition of Ti shifts the peak temperature of each parent compound to slightly lower temperature. The addition of Nb or Ta, a non-isoelectronic substitution, has substantial effects on the peak, appearing to either essentially ''wash out'' the transition or move it to temperatures above room temperature.[12] High-temperature measurements are in progress. However, in none of these substitutions (except for $Hf_{1-x}Ti_xTe_5$, $x = 0.05$) is the peak enhanced by more than a few percent, which is within the sample-to-sample variations of a given batch. Early Hall measurements concurred with the thermopower measurements as to the sign of the dominant carriers in the

system, with very similar temperature dependence.[13] These measurements indicated a hole mobility of $\approx 2900\ \mathrm{cm^2/V\,s}$ and a carrier concentration of $1.5\times 10^{18}\ \mathrm{cm^{-3}}$ for $HfTe_5$ at 210 K.

In this paper we report a large enhancement of the resistive peak with applied magnetic field, up to 9 Tesla, with a change in normalized resistivity, $\rho(9\mathrm{T})/\rho(0)$, being approximately a factor of 3 in $ZrTe_5$ and a factor of 10 in $HfTe_5$. These effects are anomalously large given that there is no magnetic character to this resistive transition. The magnitude of the magnetoresistance (MR) compares to values that are reported for some of the recent colossal magnetoresistive (CMR) materials, with a major difference being that the pentatellurides exhibit a positive magnetoresistance.[14]

EXPERIMENTAL PROCEDURE

Single crystals of $HfTe_5$ and $ZrTe_5$ were grown in conditions similar to previously reported methods.[15] The crystal structure has been well documented.[16] A stoichiometric ratio of the materials was sealed in fused silica tubing with iodine ($\approx$5 mg/mL) and placed in a tube furnace. The starting materials were at the center of the furnace with the other end of the reaction vessel near the open end of the furnace to provide a temperature gradient. Crystals of these 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 materials are complex, long chain systems with 24 atoms in an orthorhombic unit cell. The structure of the pentatellurides is comprised of MTe_3 (M = Hf or Zr) chains which are subsequently bridged into large two-dimensional (2D) sheets by tellurium atoms. The sheets are then weakly bound to one another through a van der Waal's force, which accounts for the highly anisotropic nature of the bulk crystals. The samples grow as long thin ribbons with the growth axis along the *a* axis and the *b* axis perpendicular to the thin part of the ribbon. These materials exhibit anisotropic transport properties with the high conductivity axis being the *a* axis. Electrical contact was made using Au wires bonded to the crystal with Au paint. The iodine vapor residual on the samples prevents using Ag paint, which forms a AgI layer on the sample, preventing good electrical contact. Typical sample dimensions are 1–5 mm, 0.02 mm, and 0.1 mm in the *a*, *b*, and *c* directions, respectively.

The samples were mounted using a four-probe technique for determining the resistance. The samples were inserted into a 9 T Quantum Design Physical Property Measurement System® (Ref. 17) (PPMS) for the MR and field orientation measurements. The zero-field data was in excellent agreement with literature values and the many other samples we have measured on our different experimental apparatus. The samples were mounted on a horizontal rotator board with the magnetic-field perpendicular to the current (I) direction and the growth axis of the samples. The samples could then be rotated 360° about the *a* axis. Typical data for the dependence of the field orientation on the MR is shown in Fig. 1. The largest MR occurs with $B \parallel$ to the *b* axis of the sample (the thin ribbon direction.) Typically, the orientation was set at the maximum of the MR ($B \parallel$ to *b* and $B \perp$ to I) and the data was taken as a function of temperature at differing magnetic field levels. Magnetic-field sweeps at constant temperature were also performed and the data were in excellent agreement. Data were taken at each temperature with the temperature stabilized (to within 10 mK) and the current reversed to subtract out any thermal emf's which can potentially be quite large in these samples. The magnetic field was stabilized in a persistent mode when a measurement was made to reduce any potential noise. The temperature and magnetic field were both stabilized for the magnetic-field sweep data and the orientation sweep data measurements.

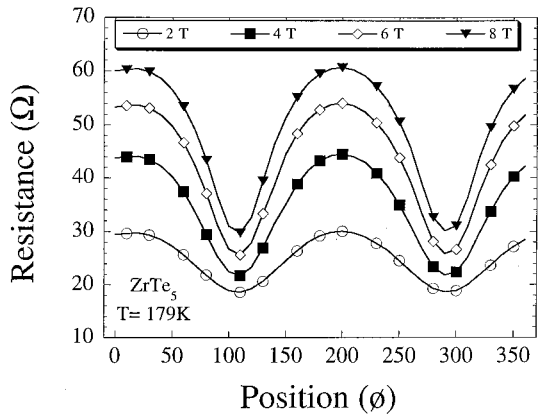

FIG. 1. Resistance at varying magnetic fields (2, 4, 6, 8 Tesla) as a function of orientation φ about the *a* axis for a single-crystal $ZrTe_5$ sample at $T = 179$ K. The maximum resistance corresponds to the $B \| b$ axis, the thin ribbon axis, and the minimum corresponds to the $B \| c$ axis. For both, the magnetic field is perpendicular to the current.

RESULTS AND DISCUSSION

As shown in Fig. 1, the MR is very dependent on the orientation to the magnetic field. The largest MR occurs when the magnetic field is parallel to the *b* axis ($B \| b$), which is the axis with the weakest bond interaction. The *c* axis is bridged between the metal chain prisms with the Te bonds which cross link between these metallic chains. The effect of an applied magnetic field is highly anisotropic and the MR can vary substantially, depending on temperature and magnetic field strength. The magnitude of the peaks (180° apart) can vary a small amount due to what we believe is a small Hall component as a result of the change in orientation. This appears, as well, in the MR as a function of temperature for at $\pm B$ (as it should be for a small Hall component).

The effect of an applied magnetic field on the resistance as a function of temperature is shown in Fig. 2 for $ZrTe_5$. There is a systematic shift of the peak temperature to slightly higher temperatures with increasing field, by approximately 25 K (145 K to 170 K) at $B = 9$ T. The most dramatic behavior is observed in relation to the magnitude of the MR around the peak. The magnetoresistance is relatively small at higher temperatures, $T > 200$ K, and increases rapidly as the temperature is lowered to near or below the peak. The magnetoresistance then decreases and undergoes another minimum before increasing again at even lower temperatures. The resistance changes approximately a factor of three between 0 and 9 T for $ZrTe_5$ near the peak temperature.

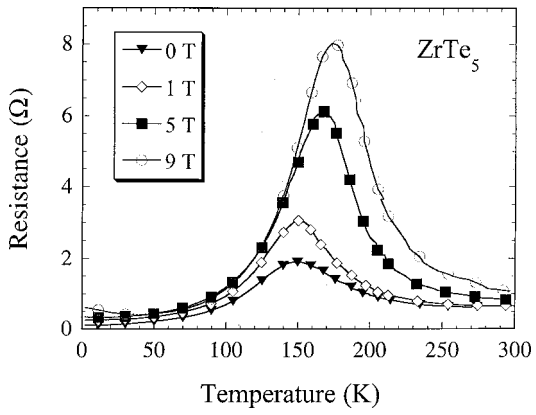

FIG. 2. Resistance of a single crystal of $ZrTe_5$ as a function of temperature for various applied magnetic fields (at $B=0$, 1, 5, and 9 Tesla, as indicated in the legend).

A similar behavior is observed in $HfTe_5$, as shown in Fig. 3. In contrast to $ZrTe_5$, only small shifts in the peak temperature are observed at low fields ($B \leq 3$ T) before this shift apparently saturates at higher fields. The magnitude of the magnetoresistance around the peak, at $B=9$ T, is approximately an order of magnitude larger than the zero-field resistance in this material. Again, the MR is relatively small at $T>145$ K and increases rapidly as the temperature is lowered near and below the peak. Similar to the magnetoresistance of $ZrTe_5$, it then decreases and undergoes another minimum before increasing again at lower temperatures. An additional difference is evident in the magnitude of the low-temperature MR in $HfTe_5$. It is approximately a factor of 200 at $T=2.5$ K and $B=9$ T and is continuing to increase in essentially a quadratic manner to our highest field values (9 Tesla), which will be discussed in more detail later.

The normalized MR $\rho(9\,\mathrm{T})/\rho(0)$, is shown in Fig. 4 for both $HfTe_5$ and $ZrTe_5$. The temperature dependence of the MR discussed previously is quite apparent. The MR is low around room temperature and increases as the temperature is lowered, reaching a peak just below T_P and undergoing a shallow minimum before increasing at lower temperatures. This is most apparent in the $HfTe_5$ material. This behavior is similar to that observed in $NbSe_3$, although the magnitude of the MR is much larger in $HfTe_5$.[8]

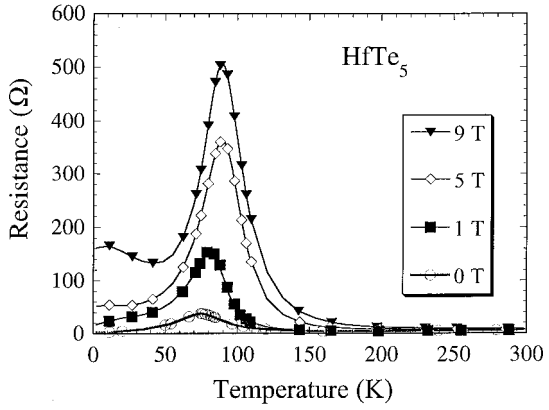

FIG. 3. Resistance of a single crystal of $HfTe_5$ as a function of temperature for various applied magnetic fields (at $B=0$, 1, 5, and 9 Tesla, as indicated in the legend).

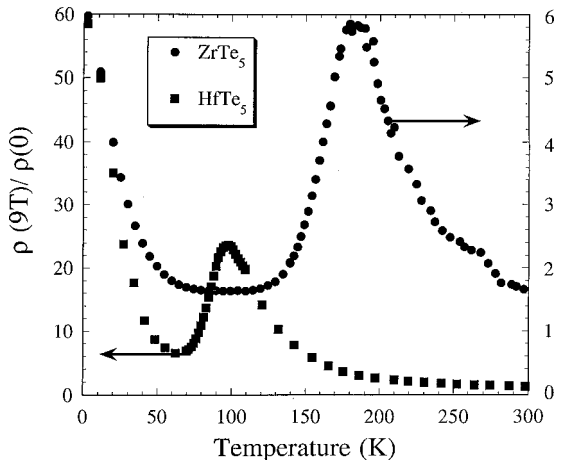

FIG. 4. Normalized magnetoresistivity, $\rho(B)/\rho(0\ \mathrm{Tesla})$, as a function of temperature for single crystals of $HfTe_5$ and $ZrTe_5$.

In $NbSe_3$ there are two CDW transitions that occur, at $T_1=145$ K and $T_2=59$ K. Below the temperature of the lower CDW transition T_2, the application of a magnetic field has a substantial effect on the resistance in this material, a large positive MR. It has essentially little or no effect on the CDW transition temperature itself and very little effect (small MR) above T_2. Early experiments and explanations coupled with theory seemed to indicate that the magnetic field was condensing normal electrons into the CDW state thus depleting them from the normal state (by as much as a 30–50 % reduction in normal carriers) and resulting in a corresponding higher resistance.[18,19] It was shown, conclusively, that the number of carriers in the CDW state was not being affected by the magnetic field, to within an experimental resolution of a few percent.[20,21] It was concluded that the large MR was due to the changing band character of the material through the CDW transition, where the normal state semimetallic character was enhanced. The system is much more semimetallic at temperatures below the CDW transition, losing a large part of its Fermi surface ($\approx$30% of the Fermi surface at T_1 and 65% of the remaining Fermi surface at T_2) and exhibits the large MR that is characteristic of narrow overlap semimetallic materials (such as Bi and Sb).[22,23] A similar explanation related to the small band overlap of semimetals may be relevant to the anomalous MR observed in these pentatelluride materials, as reported in this paper. It is apparent from the previous experiments (pressure, stress, Ti doping, as well as other transition-metal doping) that the transition is very sensitive to these parameters. It could be that one of the bands is very close to the Fermi level and small variations in energy of the system (thermal, elastic, or magnetic) can drive this band away from the Fermi level and affect the transport substantially. One of the explanations for the unusual stress dependence of the resistivity in these materials was related to the stress possibly moving one of the bands relative to the other bands and effectively emptying this band.[24] Since we do not fully understand the zero-field transport of these materials it is difficult to speculate on the origin of the large magnetoresistance. We are pursuing this question through numerous collaborations. Photoemission studies to probe the density of states in these materials are currently under way.[25] These results will be compared to existing band-structure calculations.[26,27] Obviously, much

more work is needed to further elucidate the band structure in these materials.[28]

The MR at lower temperatures ($T<25$ K) as shown in Fig. 2 exhibits some very interesting behavior. There appears to be a higher resistive state appearing below these temperatures and with increasing magnetic field. Applied stress shows an effect similar to the applied magnetic field for $T<25$ K.[26] The application of stress does not effect the magnitude of the resistive peak by more than 20% but below 25 K a high resistive state appears. This is very analogous to our previous studies of Ti doping in the $HfTe_5$ material.[13] This was an attempt to insert a smaller atom into the structure and create chemical pressure. These results could then be related to the results from the previous stress and pressure measurements. The addition of Ti increased the peak substantially, shifted it to lower temperature ($T_P \approx 40$ K with 5% Ti for Hf) and a high resistance state appeared below $T \approx 25$ K. Each of these parameters, stress, Ti substitution (pressure), and magnetic field appear to have a similar effect on the low-temperature state of $HfTe_5$ as discussed above.

SUMMARY

The application of a magnetic field produces an anomalous MR in the pentatelluride materials near the peak temperature, with $\Delta R/R$ approximately 3 in $ZrTe_5$ and 10 in $HfTe_5$ for $B=9$ T. These effects are very large given that there is no indication of any strong magnetic character to this resistive transition such as in the colossal MR (CMR) materials currently under investigation in many laboratories. These values are comparable to those reported for the CMR materials; but in contrast to these materials, the MR in the pentatelluride materials is positive. At small fields the peak is slightly shifted to higher temperatures but this effect appears to essentially saturate at fields above approximately 3 Tesla. It is apparent that the resistive transition (of a yet undetermined origin and nature) which occurs is very sensitive to doping, stress, pressure, and as reported here, magnetic field. It appears that the band structure of these materials may be very complicated. As stated, it is difficult to really speculate on the origin of the large MR given that we do not fully understand the zero-field behavior of these materials. In summary, the pentatelluride materials exhibit a very large MR around the peak temperature, which is itself weakly dependent on the magnetic field. More experiments are under way to further elucidate the origin of this resistive peak and to gain a more complete understanding of the electrical transport in these materials.

Note added in proof. Please see Ref. 29 for the theory of polaronic transport in transition metal pentatellurides.

ACKNOWLEDGMENTS

We would like to acknowledge support from ARO/DARPA Grant No. DAAG55-97-1-0267 and from the research funds provided (T.M.T.) from Clemson University. The PPMS system was purchased under ONR-DURIP Grant No. N00013-98-1-0271 (ONR) and cost shared by Clemson University. One of us (A.P.) acknowledges financial support from the Dean's Scholars program at Clemson University. We would like to also acknowledge fruitful discussions with Dr. G. X. Tessema and Dr. M. J. Skove.

*Author to whom correspondence should be addressed. Electronic address: ttritt@clemson.edu

[1] S. Furuseth, L. Brattas, and A. Kjekshus, Acta Chem. Scand. **27**, 2367 (1973).
[2] F. J. DiSalvo, R. M. Fleming, and J. V. Waszczak, Phys. Rev. B **24**, 2935 (1981).
[3] S. Okada, J. Phys. Soc. Jpn. **51**, 487 (1982).
[4] T. E. Jones, W. W. Fuller, T. J. Wieting, and F. Levy, Solid State Commun. **42**, 793 (1982).
[5] R. V. Coleman *et al.*, Phys. Rev. Lett. **55**, 863 (1985).
[6] S. Okada *et al.*, J. Phys. Soc. Jpn. **51**, 460 (1982).
[7] G. N. Kamm *et al.*, Phys. Rev. B **35**, 1223 (1987).
[8] G. N. Kamm *et al.*, Phys. Rev. B **31**, 7617 (1985).
[9] W. W. Fuller *et al.*, J. Phys. Colloq. C3-1709 (1983).
[10] R. L. Littleton IV *et al.*, Appl. Phys. Lett. **72**, 2056 (1998).
[11] Terry M. Tritt, Science **272**, 1276 (1996).
[12] R. T. Littleton, Terry M. Tritt, C. R. Feger, and J. Kolis (unpublished).
[13] M. Isumi, K. Uchinokura, E. Matsuura, and S. Harada, Solid State Commun. **42**, 773 (1982).
[14] See, for example, numerous papers in Proceedings of the Seventh Joint Magnetism and Magnetic Materials-Intermag Conference [J. Appl. Phys. **83** (1998)].
[15] F. Levy and H. Berger, J. Cryst. Growth **61**, 61 (1983).
[16] S. Furuseth, L. Brattas, and A. Kjekshus, Acta Chem. Scand. **27**, 2367 (1973).
[17] Quantum Design, San Diego, California.
[18] P. Parilla, M. F. Hundley, and A. Zettl, Phys. Rev. Lett. **57**, 619 (1986).
[19] C. A. Balseiro and L. M. Falicov, Phys. Rev. Lett. **55**, 2336 (1985).
[20] T. M. Tritt, D. J. Gillespie, A. C. Ehrlich, and G. X. Tessema, Phys. Rev. Lett. **61**, 1776 (1988).
[21] T. M. Tritt, D. J. Gillespie, A. C. Ehrlich, and G. X. Tessema, Phys. Rev. B **43**, 7254 (1991).
[22] A. B. Pippard, *Magnetoresistance in Metals* (Cambridge University Press, New York, 1989).
[23] D. R. Lovett, *Narrow Gap Semimetals and Semiconductors* (Pion, London, 1977).
[24] E. P. Stillwell, A. C. Ehrlich, G. N. Kamm, and D. J. Gillespie, Phys. Rev. B **39**, 1626 (1989).
[25] D. L. Mcllroy, Terry M. Tritt, R. T. Littleton IV, and M. L. Wilson (unpublished).
[26] M. H. Whangbo, F. J. DiSalvo, and R. M. Fleming, Phys. Rev. B **26**, 687 (1982).
[27] D. W. Bullett, Solid State Commun. **42**, 691 (1982).
[28] G. Mahan and M. Bartkowiak (private communication).
[29] M. Rubinstein, Phys. Rev. B **60**, 1627 (1999).