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Possible phase transition in the quasi-one-dimensional materials $ZrTe_5$ or $HfTe_5$

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The electrical resistance and static magnetic susceptibility of $ZrTe_5$, $HfTe_5$, and some of their alloys are reported. While the resistivity shows a large peak at low temperatures, other properties do not indicate an anomaly that could be associated with a suspected phase transition. Further, a single-crystal x-ray-diffraction study failed to reveal extra diffraction peaks below room temperature that might be associated with such a transition. While it is difficult to prove the nonexistence of a phase transition, the physical properties are not similar to related materials such as $NbSe_3$ or the transition-metal dichalcogenides which show charge-density-wave instabilities. Consequently, the resistive peak in these materials may not be due to a structural phase transition.

INTRODUCTION

A recent report of a large peak in the resistivity[1] of $ZrTe_5$ near 150 K prompted us to examine the electrical and magnetic properties of $ZrTe_5$, $HfTe_5$, and some related substitutional alloys. We also undertook a low-temperature x-ray-diffraction study of $ZrTe_5$ to search for evidence of a low-temperature structural phase transition. Our interest stemmed from the possibility of a charge-density-wave (CDW) instability in these one-dimensional materials. The structure of $ZrTe_5$ (Ref. 2) is similar to that of $NbSe_3$,[3] which shows unusual nonlinear transport properties due to a sliding CDW,[4–6] and it was hoped that similar effects might be found in these pentatellurides. While the properties of these compounds are indeed peculiar, we have been unable to obtain any definitive evidence for the existence of a phase transition, nor have nonlinear transport properties been observed.

PREPARATION

The preparation and structure of single crystals of $ZrTe_5$ and $HfTe_5$ was previously reported.[2] We prepared crystals by iodine-vapor transport and powders of $ZrTe_5$ and $HfTe_5$ by heating in evacuated quartz tubes to 480 °C for several days. All the samples were prepared from elements of the following purity: Hf (99.9%), Zr (99.9%), Ta (99.9%), and Te (99.999%). A temperature gradient of 500 to 420 °C was used for crystal growth which occurred in the cooler zone. In all cases two different crystals with similar needlelike morphology were obtained. These were identified as the transition metal pentatelluride and elemental tellurium. The latter crystals contained only trace amounts of transition metal or iodine. These tellurium crystals had shiny smooth surfaces and were quite brittle. The pentatelluride crystals frequently had striations parallel to the needle length and produced many small-diameter fibers along the needle length when crushed or severely strained. The number of tellurium crystals produced was quite small when $ZrTe_5$ was transported, but numerous tellurium crystals were observed in almost every other case.

Transport techniques were essential to produce homogeneous mixed-metal alloys when compounds were prepared from the elements. Attempts to prepare alloys such as $Zr_{1-x}Hf_xTe_5$ *or* $Zr_{1-x}Ta_xTe_5$ as powders resulted in mixtures of binary phases. Apparently, diffusion of the metallic species is quite slow below the decomposition temperature of the pentatellurides ($\approx 500-550\,^{\circ}C$). The mixed crystals produced by this method are labeled by their nominal starting composition.

MEASUREMENTS AND RESULTS

The electrical resistance was measured by the usual four-point technique. An ultrasonic soldering iron was used to completely cover the ends of the needle-shaped crystals with indium metal to ensure uniform current distribution in the crystal. The voltage contacts were made with silver paint. The resistance was measured using lock-in techniques at low frequencies (28 to 280 Hz) and measurements of the ac resistance with large applied dc voltages were obtained as previously described for $NbSe_3$.[6]

Magnetic measurements were obtained by the Faraday method. The susceptibility was measured at eight different field strengths between 2.4 and 12.8 kG to ensure that no ferromagnetic contaminants were present in the samples.

The electrical resistance from 4.2 to 300 K of $ZrTe_5$ with the current along the needle axis is shown in Fig. 1. The large peak in resistance is similar to those observed in[7] $TiSe_2$ or[4-6] $NbSe_3$ near their respective second-order phase transitions. These data are in agreement with those reported for $ZrTe_5$ by Wieting *et al.*[1] and more recently by Okada *et al.*[8] The temperature derivative is also shown as a dashed line, but no sharp breaks or peaks suggesting a particular phase-transition temperature are observed (as is the case in $TiSe_2$,[7] for example). The resistivity ρ at 300 K is approximately 5.5×10^{-4} Ω cm, with an estimated uncertainty of $\pm 15\%$ due to the somewhat nonuniform cross section of the crystals and to the physical size of the voltage contacts. At low temperatures (below ~ 70 K) the resistivity is proportional to the square of the temperature, suggesting that carrier-carrier scattering is dominant.

Similar data for $HfTe_5$ is shown in Fig. 2. The peak is larger than in $ZrTe_5$ and occurs at a lower temperature (50 K for $HfTe_5$ and 143 K for $ZrTe_5$ in Fig. 1). Again the derivative does not show any sharp structure, and $\rho(300\text{ K}) = (4.0 \times 10^{-4}$ Ω cm) $\pm$ 15%. The data reported here are similar but not identical to those obtained by Izumi *et al.*[9] The resistivity of their $HfTe_5$ samples peaks at about 76 K and their magnitude of resistivity at 200 K is about a factor of 10 larger than that reported here. Further, they observe considerable sample dependence in the magnitude of the peak $[R_{max}/R(300\text{ K})$ from about 3 to 7] but no corresponding change in the temperature at which the peak occurs (see below). Since $HfTe_5$ has a larger peak in resistivity than $ZrTe_5$, we attempted to look for an electric-field-dependent conductivity, as was seen in $NbSe_3$, in $HfTe_5$. However, no change ($< 1\%$) in ac resistance was seen at the peak (50 K) for applied dc fields of up to 1.5 V/cm, more than 2 orders of magnitude above the minimum depinning fields observed in $NbSe_3$.[6]

The size and temperature of the maximum in resistivity for both $ZrTe_5$ and $HfTe_5$ are somewhat sample dependent as clearly shown previously for $ZrTe_5$.[8] For example, for $HfTe_5$ we have observed values of $R_{max}/R(300\text{ K})$ between 8 and 10, with maxima occurring at 55 to 46 K, respectively.

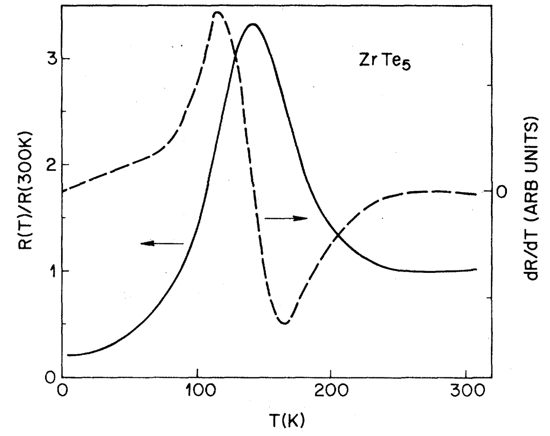

FIG. 1. The electrical resistance (solid line) and its derivative (dashed line) of $ZrTe_5$ is shown from 4.2 to 300 K. The current is parallel to the crystalline needle axis (i.e., parallel to the one-dimensional Zr chains).

The magnetic susceptibility of powders of $HfTe_5$ and $ZrTe_5$ is shown from 4.2 to 500 K in Fig. 3. The data have been corrected for small Curie contributions due to low levels of paramagnetic impurities. (The actual measured susceptibility at low temperatures is shown by the dashed line.) While the minimum in the susceptibility of $ZrTe_5$ occurs at the same temperature as the peak in the resistivity observed in single crystals, this is clearly not so for $HfTe_5$. The measured susceptibilities of the compounds at 300 K are somewhat higher than those previously reported[2] or those obtained from single crystals with the magnetic field perpendicular to the needle length.[10] However, it might be expected that

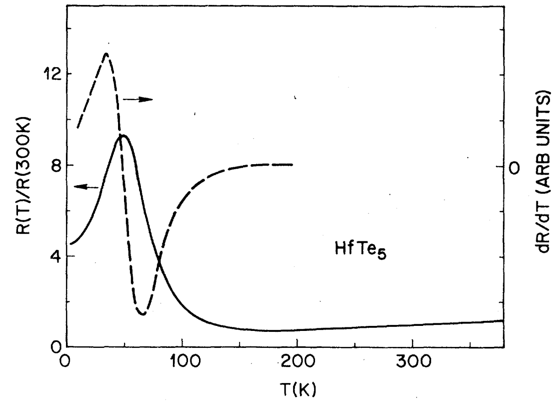

FIG. 2. The electrical resistance (solid line) and its derivative (dashed line) of $HfTe_5$ is shown from 4.2 to 300 K (with the current parallel to the Hf chains).

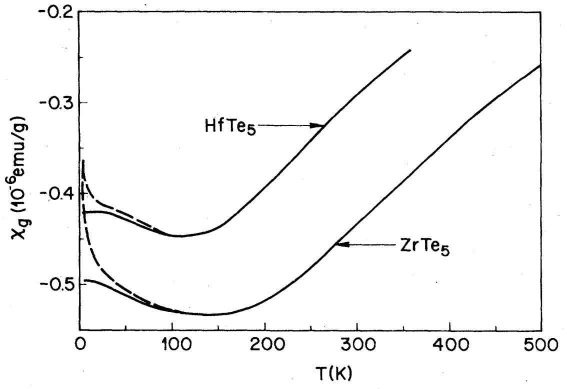

FIG. 3. The magnetic susceptibility of ZrTe$_5$ and HfTe$_5$ powder is shown from 4.2 to 500 K. The measured susceptibility at low temperatures (dashed line) is corrected for a small Curie contribution due to paramagnetic impurities.

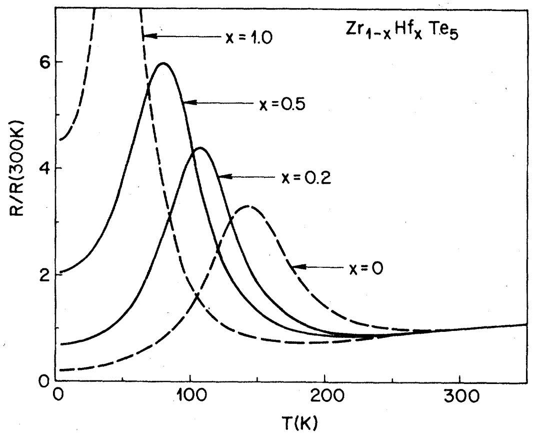

FIG. 4. The electrical resistance of Zr$_{1-x}$Hf$_x$Te$_5$ [each normalized to R (300 K)] is shown for different compositions from 4.2 to 300 K.

the susceptibility is anisotropic in these crystals so that the values obtained would depend upon the crystal orientation or randomness (or lack thereof) of the power-particle orientations. Finally we note, however, that both the temperature dependence above 200 K and the absolute difference between the susceptibilities of HfTe$_5$ and ZrTe$_5$ are in reasonable agreement with published data.[2]

We also measured the resistivity of several alloy systems of these pentatellurides: Zr$_{1-x}$Hf$_x$Te$_5$, Zr$_{1-x}$Ta$_x$Te$_5$, and Hf$_{1-x}$Ta$_x$Te$_5$. The motivation for such experiments comes again from the similarity of the pentatelluride resistance to that of TiSe$_2$ or NbSe$_3$. In both of these materials the resistive anomaly is rapidly removed by alloying, since cation disorder rapidly suppresses the phase transitions,[11,12] even if the cations are isoelectronic.[12,13] The resistance of single crystals of Zr$_{1-x}$Hf$_x$Te$_5$ is shown in Fig. 4. It is quite clear that this property evolves smoothly as a function of Hf content. Such behavior is not expected if the resistive anomaly (peak) is the signature of a phase transition. However, these data as well as the lack of sharp structure in the derivative of the resistance (Figs. 1 and 2) do not *conclusively* rule out the possibility of a phase transition. It is possible that the nature of this suspected phase transition is not at all similar to that of TiSe$_2$ or NbSe$_3$ (i.e., it is not a CDW) and thus the effects of alloying may be dissimilar. Further, it is possible that the distribution of Zr and Hf is not completely random, although powder x-ray diffraction shows diffraction lines that are sharp (instrumental width).

While the alloying of ZrTe$_5$ and HfTe$_5$ seems to have little effect on the existence of the anomaly, the inclusion of Ta has a drastic effect as shown in Fig. 5 for Zr$_{1-x}$Ta$_x$Te$_5$ and in Fig. 6 for Hf$_{1-x}$Ta$_x$Te$_5$. In these cases in particular, we emphasize that the indicated compositions are nominal in that they represent the composition of the powder from which crystals were grown. It seems likely that the pentatellurides are semimetals or even degenerate semiconductors, since the resistivity is higher than expected for a metallic compound of this kind (usually -10^{-4} Ω cm near 300 K, so the resistivity is 5 times larger than expected for a metal). Thus, it might be expected that Ta substitution would rapid-

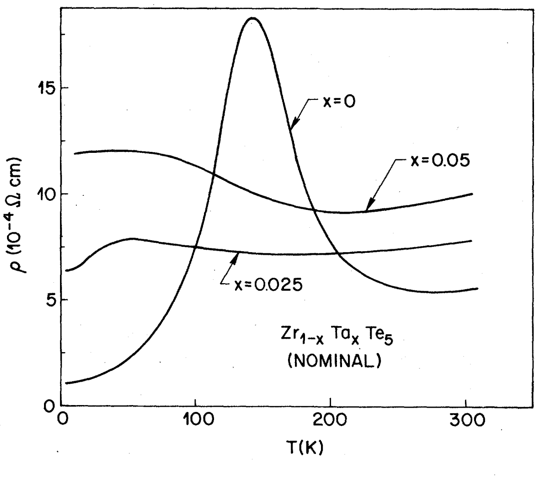

FIG. 5. The peak in the resistance of ZrTe$_5$ is removed by the substitution of Ta for Zr. (The substitutional nature of this additive is assumed, since similar substitutional behavior is observed in related trichalcogenides and dichalcogenides.)

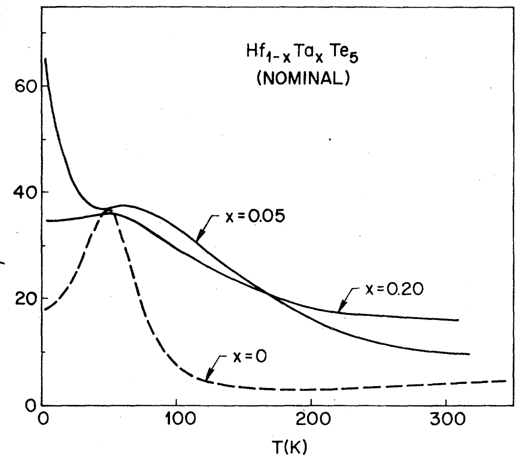

FIG. 6. The peak in the resistance of $HfTe_5$ is greatly modified by the substitution of Ta. The large value of resistivity at low temperature for $x = 0.05$ is probably due to disorder-induced localization.

ly change the conductivity characteristics of the parent compounds, since Ta would add an extra electron to the conduction band. Consequently, the changes produced by Ta may not be related to the possible presence of a phase transition.

Since the transport and magnetic data appear inconclusive concerning the possibility of a phase transition, we attempted to find a superlattice or crystalline distortion that might be caused by such a transition. A low-temperature x-ray-diffraction study of $ZrTe_5$ was undertaken using a previously described high-intensity rotating anode x-ray apparatus.[5] Weak superlattice reflections with intensities of 10^{-5} of the main Bragg peak can be easily detected by this technique. The unit cell of $ZrTe_5$ is orthorhombic[2] and contains chains of Zr atoms that are parallel to the a axis. Three of the five Te atoms form a trigonal prism about each Zr atom, and the remaining two Te atoms are bonded together and to the chains so that the chains are linked together along the c direction. There is only weak bonding between the chains in the third direction (along the b axis). Since any CDW distortion would be expected to modulate the structure along the chain (i.e., the CDW wave vector is expected to have a component along a^*), the $ZrTe_5$ crystal was mounted so that the scattering plane was $(hk0)$. Long scans taken at 80 K along [100] and [010] directions did not reveal any unexpected diffraction peaks. In scanning over restricted sections of the $(hh0)$ plane, extra diffraction peaks were observed at (2.5,0.5,0), (1.5,0.5,0), (1.5,1.5,0), (1.5,−0.5,0), and (2.5,1.5,0), which indicates that a superlattice with a reduced wave vector of $\vec{q} = (0.5,0.5,0)$ is present. These peaks remained when the crystal was warmed to 300 K, showing that the actual unit cell is doubled along the a and b axes. The intensity of the strongest of these extra reflections was about $\frac{1}{400}$th of the strongest Bragg peak [the (200) peak] in this region of the $(hk0)$ plane. Consequently, the distortions from the original structure are likely to be small. However, these extra reflections are clearly not associated with a phase transition that produces the resistive anomaly at lower temperatures, since the superlattice reflections persist to at least room temperature. Similar extra reflections were observed at room temperature in $HfTe_5$. In these studies the strong Bragg peaks of the $ZrTe_5$ crystals studied were on the order of 30 000 counts per second. The background scattering (away from the Bragg peaks) was about 0.5 counts per second. This background is normal for crystals of similar scattering power. No change in the background intensity or distribution was observed on cooling from 300 K to well below the resistive peak. In comparison, the CDW superlattice peaks observed in crystals of $NbSe_3$ of similar scattering power have intensities as large as 10^{-2} of typical Bragg peaks and 4×10^2 above background scattering. However, the present scans were taken over a restricted but representative portion of reciprocal space. It is possible that due to structure factor effects the extra peaks expected from a phase transition are extremely weak in these sections of reciprocal space. Consequently, this diffraction experiment cannot conclusively rule out the possibility of a phase transition—yet it is highly suggestive that one does not occur. However, a recent low-temperature electron-diffraction study, which examines a large portion of reciprocal space, also has failed to reveal any extra reflections that would be associated with a phase transition.[10]

SUMMARY

While the peak observed in the resistivity of $ZrTe_5$ and $HfTe_5$ suggests that this anomaly is connected with a phase transition, as in $NbSe_3$ or $TiSe_2$ for example, we have found no conclusive evidence for such a transition. The derivative of the resistance shows no sharp structure that would indicate a (probably second-order) phase-transition temperature. Further, the effects of alloying are not what would be expected if a CDW phase transition were indeed responsible for the resistive anomalies. The magnetic susceptibility, while temperature dependent, again indicates no sharp structure that would be expected if the phase transition had an electronic origin or if the crystallographic unit cell changed in such a transition. Finally, no superlattice peaks were observed at low temperatures by x-ray diffraction. Strictly speaking, it is impossible to prove that no phase transition exists in a specific material. In general, only upper limits on the magnitude of physical changes that could occur can be given. In the case of these pentatellurides, their quasi-one-dimensional structure suggests the possibility of a CDW phase transition similar to that in the related compound $NbSe_3$. Other than the peak in the electrical resistivity, the other measurements do not suggest that such a phase transition exists. However, it is possible that a phase transition due to a mechanism other than CDW's does occur, leading to different effects in some of the properties of the pentatellurides when compared to, for example, $NbSe_3$. Or the chemical and physical effects of metal substitution could turn out to be considerably different from those in all other CDW unstable materials.

If indeed there are no phase transitions in these compounds, how could the resistive anomaly be explained in these pentatellurides? It does seem possible that these materials are semimetals with a small band overlap and a subsequent temperature dependence of the carrier densities and/or mobilities. However, further data, such as the temperature-dependent Hall coefficient and perhaps the pressure dependence of the resistivity, would be necessary to show that such a model is a likely explanation for the unusual electrical properties of these pentatellurides.

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