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THERMOELECTRIC REFRIGERATION FOR TEMPERATURES BELOW 100 K:
A STUDY OF TITANIUM SESQUIOXIDE

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Previous measurements of the specific heat of V-doped Ti_2O_3 at low temperatures could be explained by a model which also suggested the material would have a high thermoelectric figure-of-merit. This paper describes the sample preparation, experimental apparatus, and the results of measurements on the thermal conductivity, thermoelectric power, and electrical resistivity of a single crystal Ti_2O_3 - 4% V sample. The results are used to derive the thermoelectric figure-of-merit between 5 and 300 K. The figure-of-merit is much smaller than expected and of little practical value because of the very high phonon thermal conductivity.

Key words: cryogenics; figure-of-merit; refrigeration; resistivity; thermal conductivity; thermoelectric power; Ti_2O_3 ; vanadium.

1. INTRODUCTION

Thermoelectric refrigeration of small devices has the advantage of extreme reliability which cannot be matched by any other refrigeration technique. Thermoelectric coolers have demonstrated a MTBF (mean time between failure) in excess of 300,000 hours which is equivalent to 35 years of continuous operation. For temperatures considerably below room temperature thermoelectric devices achieve a coefficient of performance (COP) of only 1-2% but this low efficiency is of little concern for cooling of small devices where the total power input may be only 50 W. Presently the lowest temperature achieved with a multiple stage thermoelectric cooler is about 134 K [1,2]. Click and Marlow [3] reached 145 K in a similar refrigerator. In each stage the maximum temperature drop is given by [4]

$$(T_h - T_c)/T_c = 1/2 ZT_c, \quad (1)$$

where T_h is the hot temperature, T_c is the cold temperature, and Z is the thermoelectric figure-of-merit. For a single material Z is given by

$$Z = \alpha^2/k\rho, \quad (2)$$

where α is the thermoelectric power, or Seebeck coefficient, k is the thermal conductivity, and ρ is the electrical resistivity. In an actual refrigerator the figure of merit for a junction of material 1 and 2 is

$$Z_{12} = (\alpha_1 - \alpha_2)^2 / [(k_1 \rho_1)^{1/2} + (k_2 \rho_2)^{1/2}]^2. \quad (2a)$$

The largest values of Z_{12} occur when α_1 and α_2 are large and of opposite sign. Thus in practical refrigerators the junctions are made with an n-type material (negative α) and a p-type material (positive α).

Figure 1 shows the highest reported values of Z as a function of temperature for several thermoelectric materials. Shown for comparison is a curve for $ZT = 1$. Temperature drops for each stage according to eq (1) become quite small for ZT much less than 1. For refrigeration just below room temperature the Bi_2Te_3 alloys are used in both the n and p legs of the couple. Values of Z for these two Bi_2Te_3 alloys are from the work of Yim et al. [5] and Yim and Rosi [6]. The n-type Bi_2Te_3 alloy is $(\text{Bi}_2\text{Te}_3)_{90}(\text{Sb}_2\text{Te}_3)_5(\text{Sb}_2\text{Se}_3)_5$ doped with SbI_3 to give a carrier concentration of $3.6 \times 10^{-19} \text{ cm}^{-3}$ at room temperature. The p-type material is $(\text{Sb}_2\text{Te}_3)_{72}(\text{Bi}_2\text{Te}_3)_{25}(\text{Sb}_2\text{Se}_3)_3$ doped with excess Te to give a carrier concentration of $2.1 \times 10^{-19} \text{ cm}^{-3}$ at room temperature. The Z value for these Bi_2Te_3 alloys is reasonably high at room temperature but it falls off rapidly at low temperatures, especially that of the p-type material. By changing the doping levels Click and Marlow [3] were able to increase the Z value of the p-type Bi_2Te_3 alloy at low temperatures as shown in figure 1. This is the highest reported Z value for a p-type material below 220 K. For n-type materials figure 1 shows that the low temperature Z values are much higher. The data for undoped $\text{Bi}_{85}\text{Sb}_{15}$ and $\text{Bi}_{92}\text{Sb}_8$ are from the work of Yim and Amith [7] and is the highest reported Z value for any material. Wolfe and Smith [8] first showed that the application of a transverse magnetic field can enhance Z significantly in Bi-Sb alloys. Yim and Amith [7] applied a transverse field of 1T to their $\text{Bi}_{85}\text{Sb}_{15}$ sample and obtained the results shown in figure 1. Higher fields will not increase the peak value but they can increase the higher temperature Z values. Figure 1 shows that at intermediate temperatures the $\text{Bi}_{92}\text{Sb}_8$ alloy doped with $1 \times 10^{18} \text{ cm}^{-3}$ of Sn gives the best Z values [3]. Low-temperature thermoelectric refrigeration is severely hampered by the lack of a good p-type material below 200 K. The purpose of this program was to investigate the thermoelectric figure-of-merit for a p-type material which showed potential for a high Z .

2. NEW MATERIALS

The electronic part of the Seebeck coefficient is simply proportional to the electron molar entropy S and is given by

$$\alpha = (8.6 \times 10^{-5} \text{ V/K}) S/R, \quad (3)$$

where R is the gas constant. For ideal electrons $S/R = 2.9$ at the Fermi temperature T_F and it is linear in T somewhat below T_F . The entropy can be determined from specific heat measurements through the relation

$$S(T) = \int_0^T (C/T') dT', \quad (4)$$

where C is the specific heat and T' is the temperature. Thus, a material with a high electron or hole entropy would be a good candidate material if the carrier concentration is relatively high to give a

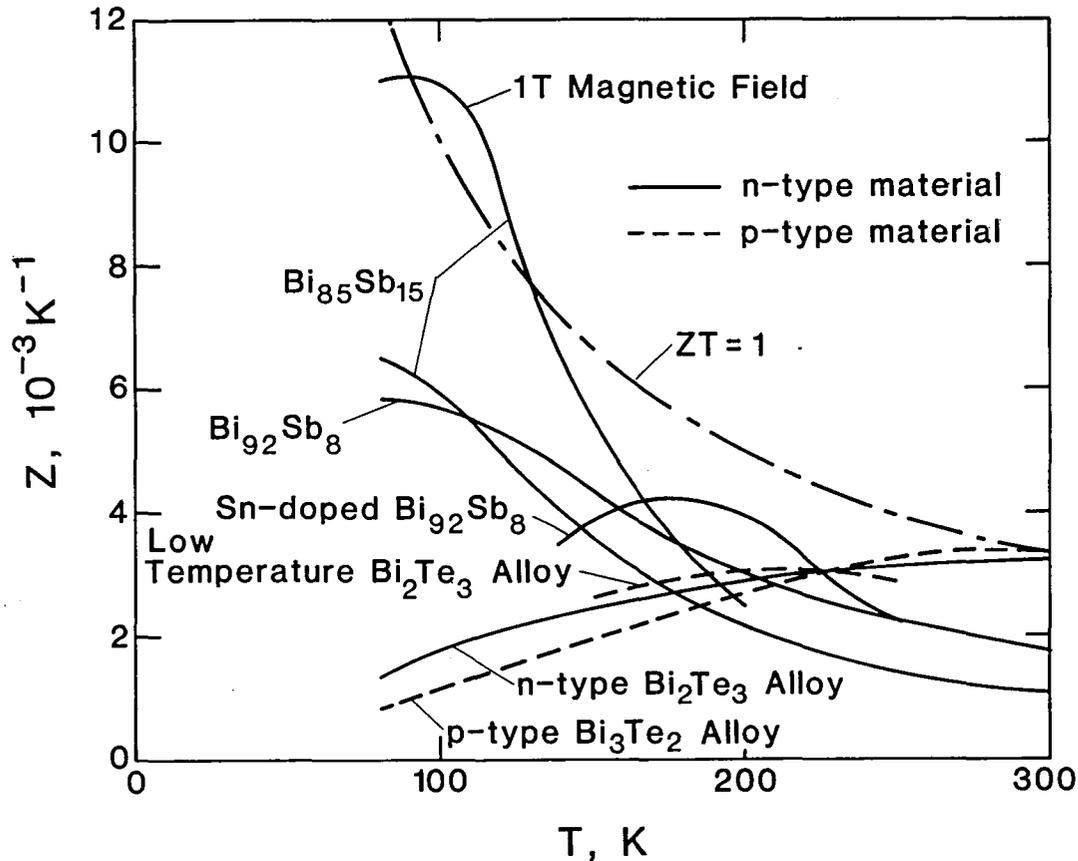


Figure 1. Thermoelectric figure-of-merit, Z , as a function of temperature for several high Z materials. Exact compositions are discussed in the text.

low resistivity. Pure metals have such high T_F ($\sim 6 \times 10^4$ K) that the electron entropy is very small below room temperature. Pure bismuth has a T_F of about 5 K [4], but the carrier concentration is only $3 \times 10^{17} \text{ cm}^{-3}$.

Sjöstrand and Keesom [9] measured the low temperature specific heat of vanadium doped titanium sesquioxide, Ti_2O_3 , and found an anomalously large specific heat and entropy. They could explain their data by using an electron gas model with a Fermi temperature of about 5 K for the sample with 4% V doping. The carrier concentration is about 10^{20} cm^{-3} , which is much higher than that of bismuth. These results then prompted the proposal which led to this work. Dumas et al. [10], however, have suggested that the high specific heat is mainly due to a spin glass behavior of a magnetic moment on the vanadium impurity. If that explanation is correct the figure-of-merit would not be high unless the carriers can interact with the spins in such a way to sample their entropy.

Previous measurements on the thermoelectric power of V-doped Ti_2O_3 by Shim et al. [11] only extend down to about 55 K. For 4% V their results show a nearly constant value of about $+50 \mu\text{V/K}$; for a 2% V sample they find $+100 \mu\text{V/K}$. The positive value indicates the material is p-type. Resistivity measurements [12] on a different sample of $\text{Ti}_2\text{O}_3 + 4\% \text{V}_2\text{O}_3$ give a value of about $5 \times 10^{-4} \Omega \text{ cm}$ below 100 K. No measurements of thermal conductivity have been made to date. Using the Wiedemann-Franz law for the thermal conductivity would give a figure-of-merit

$$Z = \alpha^2 / L_0 T, \quad (5)$$

where the Lorenz ratio $L_0 = 2.44 \times 10^{-8} \text{ V}^2/\text{K}^2$. For $\alpha = 100 \text{ } \mu\text{V}/\text{K}$, $ZT = 0.40$. Lower V concentrations increases α significantly but the phonon contribution to the thermal conductivity could dominate at low V concentrations and prevent any increase in Z.

A single crystal of $\text{Ti}_2\text{O}_3 - 4\% \text{ V}_2\text{O}_3$ was received from Prof. Keesom of Purdue University. This sample was not the same as the one on which they measured the specific heat. X-ray pictures were taken here to orient the sample since there could be some orientational dependence in the figure-of-merit. A diamond saw was used to cut the sample to be measured. The sample size was about 1.5 mm x 2.0 mm x 10 mm with the long dimension along the a axis of the crystal. The crystal type for Ti_2O_3 is rhombohedral [13] with $a = 5.433 \text{ \AA}$ and $\phi = 56^\circ 34'$.

3. EXPERIMENTAL APPARATUS

The figure-of-merit is determined from measurements of α , k , and ρ in eq (2). Figure 2 shows a schematic of the apparatus built to measure these three quantities simultaneously. Not shown in this figure are the current and voltage leads to the sample. The voltage leads are placed at the same points along the sample as are the sample thermometers, except they are on the adjacent face. The carbon thermometers are 220 Ω , 1/8 W resistors which have been ground flat on one side. These resistors are then varnished to a small copper clamp with cigarette paper providing electrical insulation between resistor and clamp. These clamps also have the junctions of a differential thermocouple mounted on them with varnish. The clamp closest to the reservoir also has another thermocouple junction to measure the temperature difference between that junction and one in the liquid cryogen bath outside the vacuum can. The thermocouples used are Au-0.07at% Fe versus KP [14]. The carbon thermometers are used for temperatures from 4 K up to about 50 K and the thermocouples are used from 50 K up to 300 K. The carbon thermometers were calibrated against a germanium thermometer that was mounted on the bottom of the reservoir. The R vs. T characteristic of the carbon thermometers were then fit to a power series of the form

$$\log T = \sum_{i=0}^N a_i (\log R)^i. \quad (6)$$

The best fit was obtained when the curve was divided into two parts: one part below 20 K and the other part above 20 K. Usually four terms were sufficient for a good fit.

We used silver paint to attach the voltage and current leads to the sample. The very small size of the sample made it difficult to work with and the accuracy of the thermometer and voltage tap spacing was probably no better than $\pm 10\%$.

The procedure for making the measurements was to first fill the reservoir with liquid helium from the outside bath. With no heat applied to the sample heater, the resistances of the carbon and germanium thermometers were measured using a commercial AC potentiometer. Next a small AC current was passed through the sample and the voltage drop between the potential leads was determined with a lock-in amplifier. The lock-in amplifier was also used to measure the voltage drop across a 0.1 Ω standard

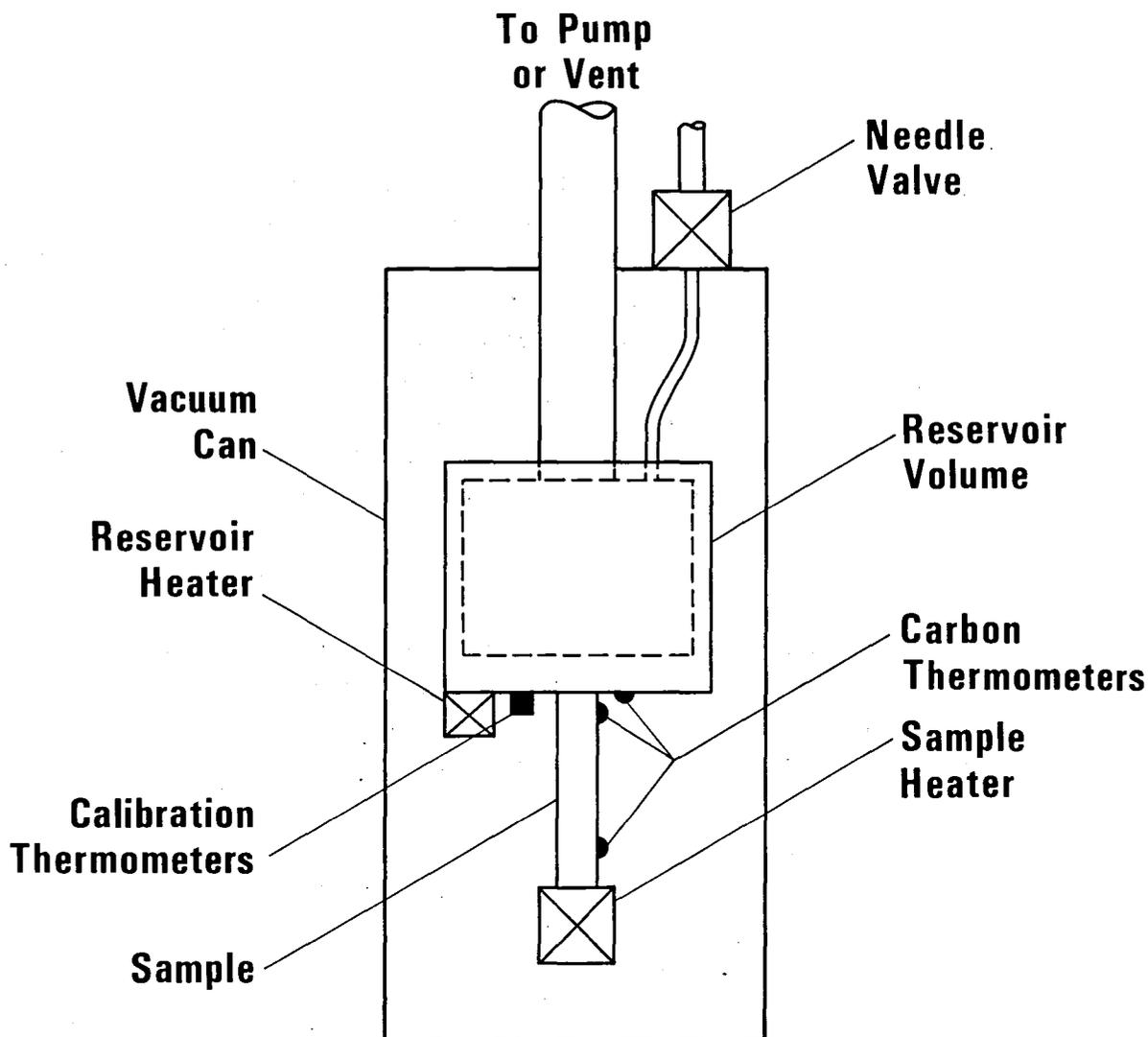


Figure 2. Schematic diagram of the apparatus used for simultaneous measurements of thermal conductivity, thermoelectric power, and electrical resistivity. Liquid helium or liquid nitrogen surrounds the vacuum can. The temperature of the reservoir volume is regulated by the needle valve and a commercial temperature controller supplying current to the reservoir heater.

resistor in series with the sample to give the current passed through the sample. These readings then gave the resistivity of the sample. The next step was to apply a known current to the sample heater and record the thermometer readings to derive the temperature gradient in the sample. The thermal conductivity is then obtained from

$$k = \dot{Q}L/A \cdot \Delta T, \quad (7)$$

where \dot{Q} is the heat flow through the sample, L is the length between the two thermometers, and A is the cross-sectional area of the sample. Usually the ΔT was about 5-10% of the absolute temperature.

At the same time that the thermometers were being read, the voltage between the potential taps was measured with a sensitive digital voltmeter to give the thermoelectric power of the sample according to the equation

$$\alpha = \Delta V / \Delta T. \quad (8)$$

The sample heater was then turned off and power applied to the reservoir heater to bring it up to the next higher temperature. For temperatures above 4 K, there was no liquid He in the reservoir. A temperature controller was used to maintain a constant reservoir temperature while measurements were being made. For best temperature control, it was found necessary to open the needle valve slightly to provide some cooling power for the reservoir. The use of a needle valve is much more economical with liquid He than is a cryostat which has a semi-weak thermal link between the reservoir and the surrounding liquid helium bath. At higher temperatures (~ 50 K) the sensitivity of the thermocouples became high enough to use them as the thermometers instead of the carbon resistors. For temperatures above 77 K, the liquid He in the outside bath was replaced with liquid N_2 .

4. RESULTS AND DISCUSSION

Figure 3 shows the resistivity of the Ti_2O_3 - 4% V sample as a function of temperature. The curve is about 30% lower than that published by Van Zandt and Eklund [12], also for a Ti_2O_3 sample doped with 4% V. The shape of the two curves are very much the same. The difference between their curve and ours is most likely due to small differences in V doping. The uncertainty of our curve is about $\pm 10\%$.

Figure 4 shows the thermoelectric power of the sample as a function of temperature. For temperatures above about 100 K, α is independent of temperature and equal to about $60 \mu V/K$. This value is consistent with the measurements of Shin et al. [11] who measured α above 54 K for Ti_2O_3 doped with various amounts of V. Below about 50 K we find that α drops off nearly linearly with temperature. The uncertainty in α is about $\pm 10\%$ except in the region between about 15 and 40 K where difficulty in measuring a small temperature gradient gave rise to considerable scatter in the data as seen in figure 4. The thermal conductivity was very high in this region, which made it difficult to maintain a reasonable temperature gradient.

The thermal conductivity of the sample is shown in figure 5. The peak observed around 25 K was quite surprising, since we thought that with 4% V doping phonon scattering would be sufficiently high to eliminate a high peak. Previous measurements on TiO_2 (rutile) [15] showed that its peak in thermal conductivity was essentially eliminated just with a hydrogen reduction, as shown by the dashed curve in figure 5. Even the oxidized samples of TiO_2 showed a lower intrinsic thermal conductivity than our sample of Ti_2O_3 - 4% V for temperatures above about 50 K. Also shown in figure 5 is the thermal conductivity of p-type Bi_2Te_3 [5]. Uncertainty of the thermal conductivity is about $\pm 10\%$, except near the peak where the imprecision is about $\pm 20\%$ because of the difficulty in maintaining a sufficiently large ΔT with adequate temperature control.

The thermoelectric figure-of-merit for the Ti_2O_3 - 4% V sample was calculated from the ρ , k , and α curves by using eq (2). This figure-of-merit is shown as a function of temperature in figure 6.

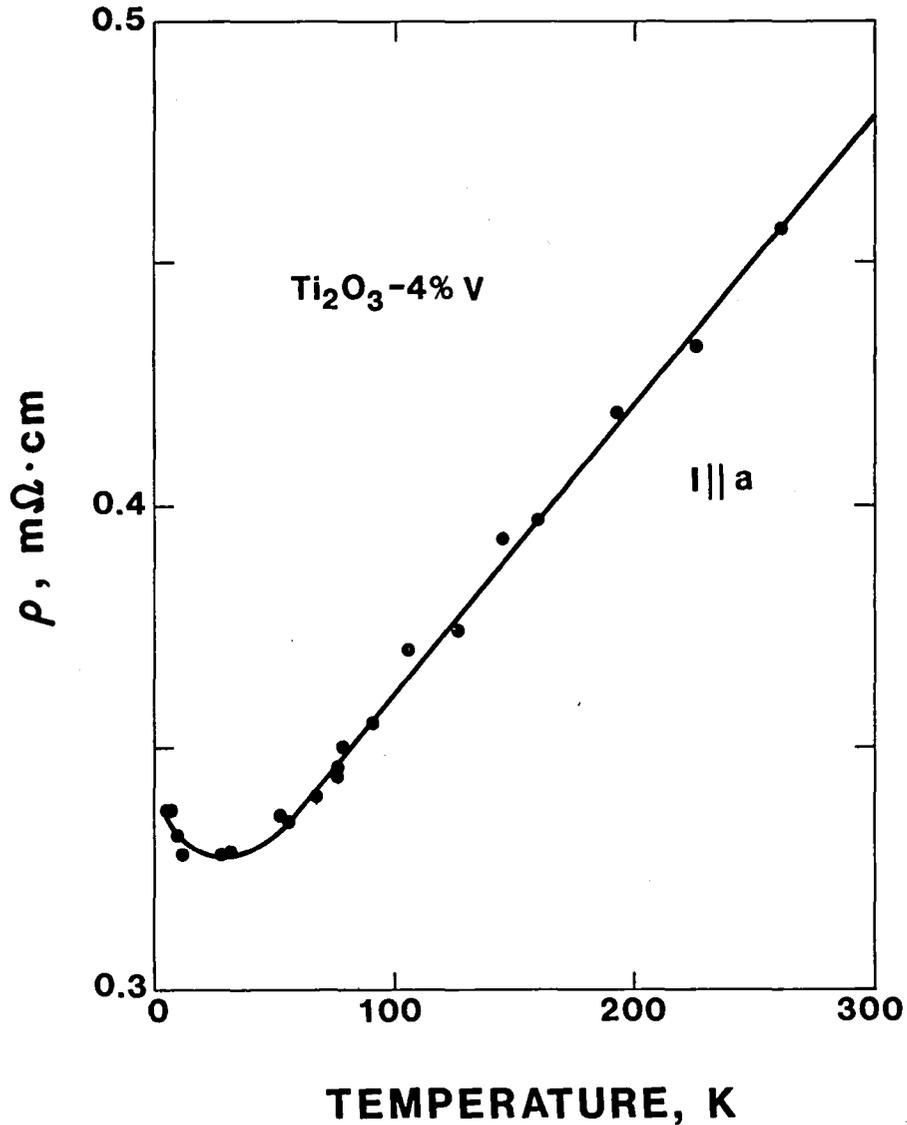


Figure 3. The electrical resistivity of $\text{Ti}_2\text{O}_3 - 4\% \text{V}$ as a function of temperature for current along the a axis of the crystal.

Shown for comparison are experimental curves for a p-type Bi_2Te_3 alloy [5] and for the Kondo systems [16] CePd_3 and CeIn_3 . We had expected that Z of the Ti_2O_3 with V doping would be higher than that of Bi_2Te_3 below about 100 K. Unfortunately the very high phonon thermal conductivity greatly reduces the figure-of-merit for Ti_2O_3 . If we were to neglect the phonon contribution to the thermal conductivity, we would then expect the Wiedemann-Franz law to be a good approximation and the figure-of-merit to be given by eq (5). The dashed curve in figure 6 for $\text{Ti}_2\text{O}_3 - 4\% \text{V}$ then gives the value expected for Z from the Wiedemann-Franz law, which represent approximately the maximum we could expect from the material.

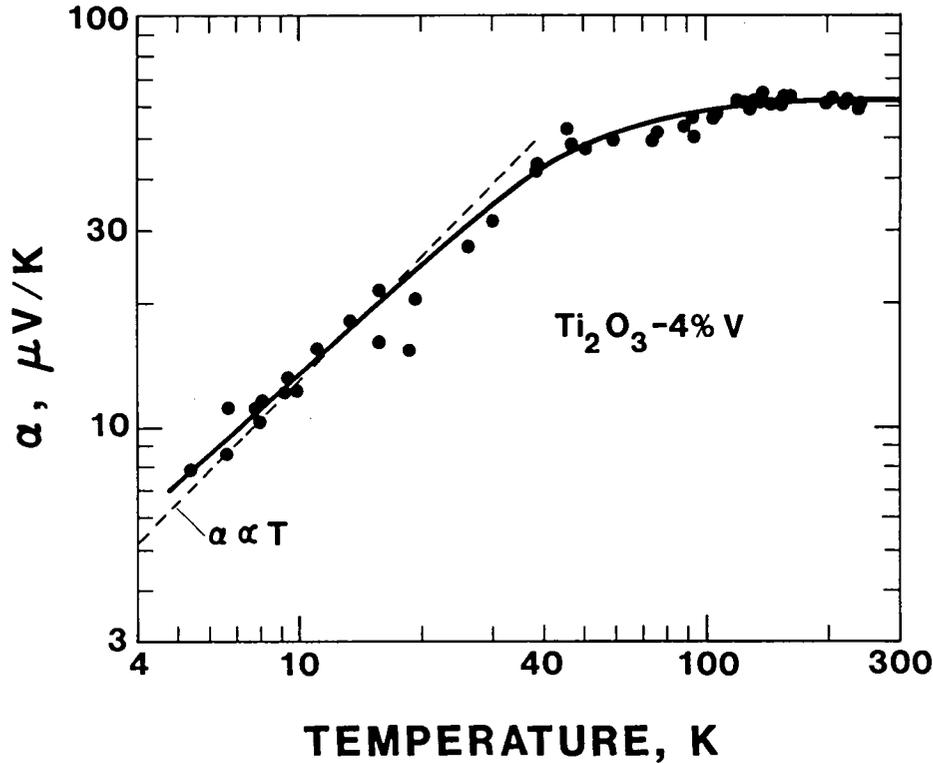


Figure 4. The thermoelectric power, or Seebeck coefficient, as a function of temperature for a Ti_2O_3 - 4% V sample. The dashed line shows a curve proportional to temperature.

From the work of Shin et al. [11], we know that lower V doping gives a higher α . For V concentrations in the range of about 1-5%, it appears that α is inversely proportional to the V concentration. Thus, according to eq (5) we would expect the figure-of-merit to increase inversely with the square of the V concentration. Figure 6 shows the expected Z for a sample with 2% V doping and with the phonon contribution to the thermal conductivity neglected. The behavior of this curve below 50 K is somewhat uncertain since we do not know the concentration dependence of α below 50 K. We did not measure α below 50 K for a 2% V sample since we did not expect that the actual Z would change much. For lower V concentrations, ρ would increase rapidly, but because the thermal conductivity is dominated by phonon conductivity, it would also increase somewhat instead of decrease.

We see from the curves of figure 6 that a Ti_2O_3 - 2% V sample could have a much larger figure-of-merit than p-type Bi_2Te_3 below 200 K if some means of greatly decreasing the phonon conductivity could be found that does not affect the carrier conductivity. We had hoped that even 2% V would have been sufficient to greatly reduce the phonon contribution, but for some reason V is not a very effective phonon scatterer in Ti_2O_3 .

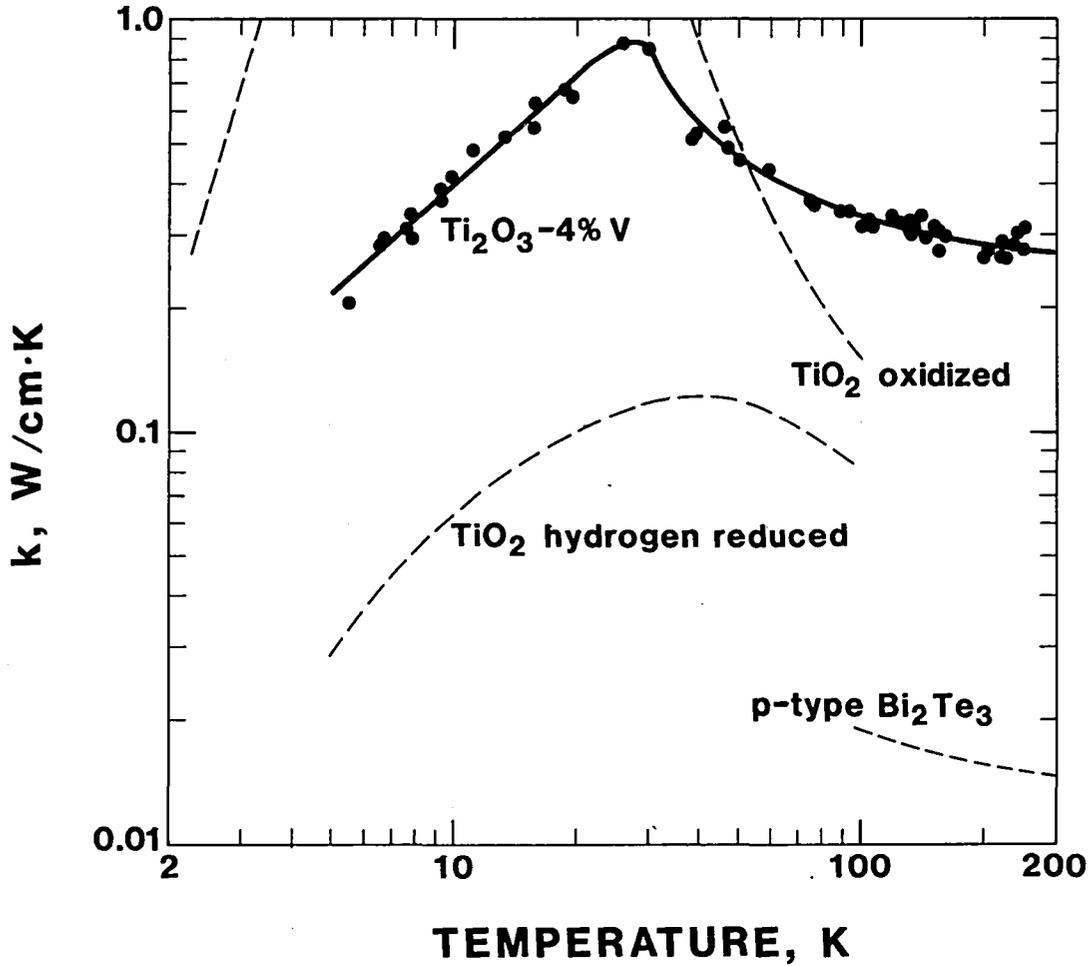


Figure 5. The thermal conductivity of $Ti_2O_3 - 4\% V$ as a function of temperature. Shown for comparison are curves for oxidized and hydrogen reduced TiO_2 (rutile), as well as p-type Bi_2Te_3 .

It is of some interest to compare α with that expected from eq (3). The specific heat measurements of Sjöstrand and Keesom [9] give $S/R \approx 0.27 T$ for the carriers in a 3.9% V sample of Ti_2O_3 at temperatures below about 2 K. Substituting this value into eq (3) gives an expected thermoelectric power of $\alpha = 23 T \mu V/K$. Experimentally we find that $\alpha \approx 1.3 T \mu V/K$. Thus, according to this comparison, it would seem that the high specific heat of the V-doped Ti_2O_3 is not due to free carriers as had been originally proposed [9]. The spin glass behavior suggested by Dumas et al. [10] would be consistent with the observed behavior of α below 50 K.

Since it is known that transverse magnetic fields can enhance the figure-of-merit in some materials [7], measurements of ρ , α , and k were made at 77 K in a transverse field of 1.2 T. There was no detectable change in any of these quantities with the field applied.

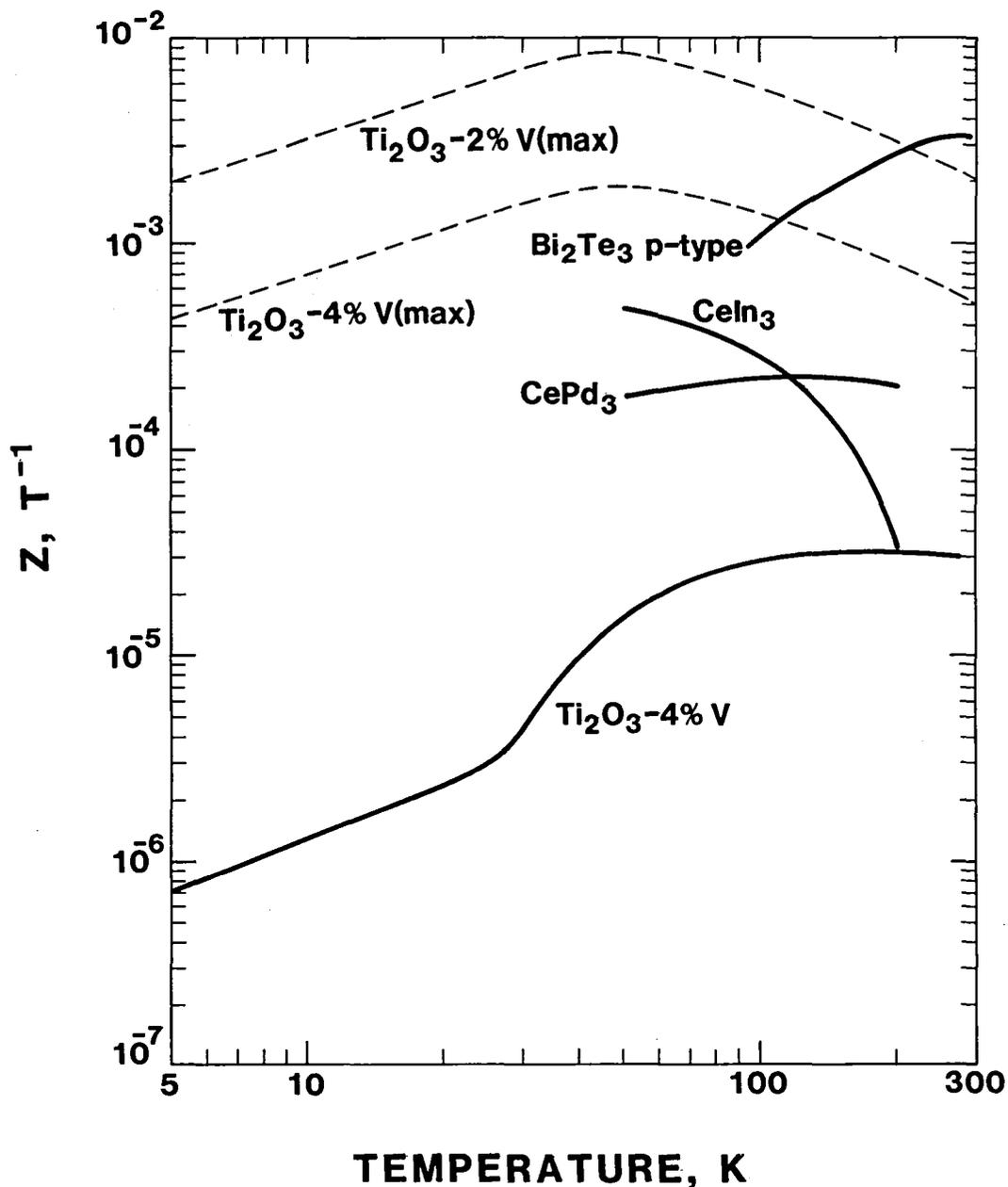


Figure 6. The thermoelectric figure-of-merit for $Ti_2O_3 - 4\% V$ as a function of temperature. The dashed curves give the figure-of-merit if the phonon conductivity were neglected. The p-type Bi_2Te_3 has the highest known figure-of-merit for any p-type material. The other curves are discussed in the text.

5. CONCLUSIONS

We conclude that contrary to initial expectations, based on the high specific heat, the thermoelectric figure-of-merit of V doped Ti_2O_3 is not sufficiently high to be of any practical value. Even for the optimum V concentration we do not expect the figure-of-merit to be as high as p-type Bi_2Te_3 . The figure-of-merit for V doped Ti_2O_3 could be greatly enhanced, and even exceed that of p-type Bi_2Te_3 , if some means could be found to greatly reduce the high phonon thermal conductivity without decreasing the carrier conductivity.

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