

THE THERMAL CONDUCTIVITY OF
SODIUM TUNGSTEN BRONZES

By

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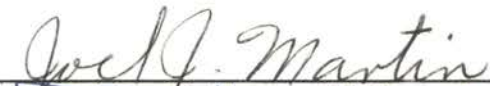
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$x = 0.78$. An anomaly was also reported in the electrical conductivity at $x = 0.75^2$. This anomaly was attributed to ordering of the sodium atoms and the formation of a superlattice.

Historical Development

The nonstoichiometric compounds, M_xWO_3 , where x takes values between zero and one, and M is an alkali metal are commonly called the alkali tungsten bronzes. Much work has been done in particular on the sodium tungsten bronzes. Sodium tungsten bronze was first produced in 1824³. The major problem in studying Na_xWO_3 has been the difficulty in obtaining homogeneous crystals.

All of the sodium tungsten bronzes have a crystal structure which is perovskite related. For x greater than 0.48 Na_xWO_3 has a cubic lattice similar to cubic barium titanate with the sodium atoms randomly distributed on the barium sites in the Na_xWO_3 unit cell. For x greater than 0.25 but less than 0.48, the lattice is the tetragonal I structure. For x greater than 0.25 they exhibit metallic transport properties such as high electrical conductivity, high thermal conductivity, and a metallic luster. For x less than 0.25 Na_xWO_3 is an extrinsic semiconductor with the tetragonal II structure.

For $x = 0.75$ six of the eight sodium sites are occupied in the unit cell. Atoji and Rundle⁴ found that ordering of the sodium atoms occurred at $x = 0.75$. Their neutron diffraction work showed that this ordering formed a superlattice with twice the lattice constant of the original unit cell. If the unit cell of the superlattice is chosen such that a sodium site is at each corner, then there are no sodium atoms at

et al.¹⁰ made extensive electrical resistivity measurements on samples with a wide range of x-values that were electrically homogeneous. They found no minimum in the resistivity at $x = 0.75$. The minimum in resistivity around $x = 0.75$ that had been reported earlier was, therefore, due to the inhomogeneity of the samples measured, and not characteristic of Na_xWO_3 .

Later work by Muhlestein and Danielson² showed that an inflection point occurs in the resistivity versus x-value curve at $x = 0.75$. This inflection point was attributed to an ordering of the sodium atoms and the formation of a superlattice. Since the lattice constant of the superlattice has been shown to be twice the original lattice constant⁴, the periodicity of the lattice potential seen by electrons would be twice the original lattice spacing. They suggested that a second conduction band would be formed with electrons of different effective mass than the original conduction band.

Muhlestein and Danielson also measured the Hall coefficient and Seebeck coefficient of Na_xWO_3 . Their results showed that a one-to-one relationship between sodium atoms and conduction electrons was not exactly true. They did, however, indicate that each sodium atom was ionized, and the deviation from the one-to-one relationship was due to the second conduction band. They used crystals that had been grown by electrolysis¹¹ from a melt of sodium tungstate (Na_2WO_4) and WO_3 . Heat treatment of the crystals under high vacuum was found to improve the homogeneity.

Only limited theoretical work has been done on the alkali tungsten bronzes. Mackintosh¹² proposed a model where the conduction electron wave functions are derived from the alkali metal atomic p functions.

Goodenough¹³ suggested that the conduction band was formed from a mixing of tungsten-oxygen orbitals (d_{π} - p_{π}). Gerstein, Thomas, and Silver¹⁴ made overlap calculations using Slater orbitals for several possible mixings of states. They found that the d_{π} - p_{π} orbitals were most favorable. It would appear then that the alkali metal acts only as an electron donor and changes the WO_3 energy bands very little.

Goodenough also made qualitative predictions concerning the ordering of sodium atoms in Na_xWO_3 at $x = 0.75$. He compared the band structure to that of ReO_3 . Rhenium has one more electron than tungsten, and ReO_3 has metallic transport properties. ReO_3 should, therefore, correspond to $NaWO_3$ ($x = 1$). For x less than 0.75 he predicted that there would be a partially filled band below the Fermi level. However, at $x = 0.75$, sodium ordering would occur, and a new band would form at or near the Fermi level.

The metallic electrical conductivity of Na_xWO_3 was attributed by Goodenough to the x electrons per unit cell from the sodium atoms in the ReO_3 related conduction bands. For x less than 0.75 the electrons occupy the partially filled band below the Fermi level. For x greater than 0.75 there are two types of carriers present: higher mobility electrons in the original band and lower mobility electrons in the new conduction band due to sodium ordering. Goodenough's model predicted that a maximum in the electrical conductivity could occur at $x = 0.75$, but that probably only a change in slope of the electrical conductivity versus x -value curve would occur. Muhlestein and Danielson found that the electrical conductivity increased more rapidly with x for x greater than 0.75. However, the inflection point predicted by Goodenough was

observed.

Low temperature measurements of the heat capacity of the sodium tungsten bronzes were made by Vest, et al.¹⁵ They found a large increase in the density of states at the Fermi level at $x = 0.75$. This increase in the density of states would support the band structure proposed by Goodenough. Annealing of their samples at 700-800°C was found to change this density of states very little, but it had a large effect on the lattice specific heat. Thus, it appeared that inhomogeneity affected the lattice heat capacity much more than the electronic heat capacity. Gerstein, Klein, and Shanks¹⁶ made high temperature heat capacity measurements on one of the samples of Vest, et al.

Now that large homogeneous single crystals of sodium tungsten bronze can be made, it is possible to make thermal conductivity measurements. Shanks and Redin¹⁷ made thermal conductivity measurements on two samples over the temperature range 350-800 K. Both samples had a positive temperature coefficient which was interpreted as a combination of electron and phonon conduction limited by impurity scattering.

Martin and Shanks¹ measured the low temperature (4-300 K) thermal conductivity of four samples ranging in x-value from 0.513-0.862. They were able to separate the measured thermal conductivity into an electronic and lattice component. The lattice component of their $x = 0.862$ sample showed a temperature dependence that was reasonable for lattice conduction. The lower x samples, however, had an apparent lattice component that deviated from normal lattice conduction.

CHAPTER II

EXPERIMENTAL MEASUREMENTS

Thermal Conductivity

The flow of heat through a substance can be represented by the equation

$$Q = \lambda \, dT/dx \quad (1)$$

where Q is the heat energy crossing unit area per unit time, dT/dx is the temperature gradient in the direction of heat flow, and λ is the thermal conductivity of the substance. For a long rod of uniform cross-sectional area A the thermal conductivity can be represented by

$$\lambda = (W/A) (dx/dT) \quad (2)$$

where W is the power supplied to one end of the rod. In practice the temperature gradient is found by measuring the temperature difference at two points separated by some distance L . Thus,

$$\lambda = (L/A)W/(T_1 - T_2) \quad (3)$$

Thermal conduction in a substance is due to two different mechanisms. For a metal heat can be conducted by both conduction electrons and lattice vibrations (phonons). Experiment has shown that for pure metals nearly all the heat is carried by electrons. For impure metals, alloys, and semiconductors a measurable portion of the thermal conductivity is due to phonons. In insulators all the heat conduction is due to phonons. Mendelssohn and Rosenberg¹⁸ have reviewed the thermal con-

This relation is valid in the region of room temperature for a large number of metals and high conductivity alloys. A Lorenz ratio higher than L_0 , however, is common in the transition metals and in low purity alloys.

Phonons are scattered by lattice distortions or at low temperatures by crystal boundaries. Phonon-phonon interactions are important at temperatures such that the magnitude of the sum of the phonon momenta is equal to the magnitude of a reciprocal lattice vector. The thermal conductivity of a solid may be affected by several scattering mechanisms in a particular temperature range.

Apparatus

The apparatus employed a standard steady-state heat flow technique. The sample holder is shown in Figure 1. The sample was clamped at one end to a copper clamp which made good thermal contact with a copper rod. This rod acted as a heat sink. A stainless steel tube of slightly larger diameter was fitted over the copper rod. The small space between rod and tube could be filled with helium gas to adjust the thermal contact of the heat sink with the liquid in which the sample holder was immersed.

The sample and lower half of the heat sink were vacuum sealed in a brass can. The vacuum seal was made with a low melting indium alloy solder. All measurements were made with a pressure lower than 10^{-5} torr. It was assumed that all heat dissipated by the heaters must flow along the heat sink to reach the liquid bath. Liquid helium was used as the bath for temperatures less than 50 K, and liquid or solid nitro-

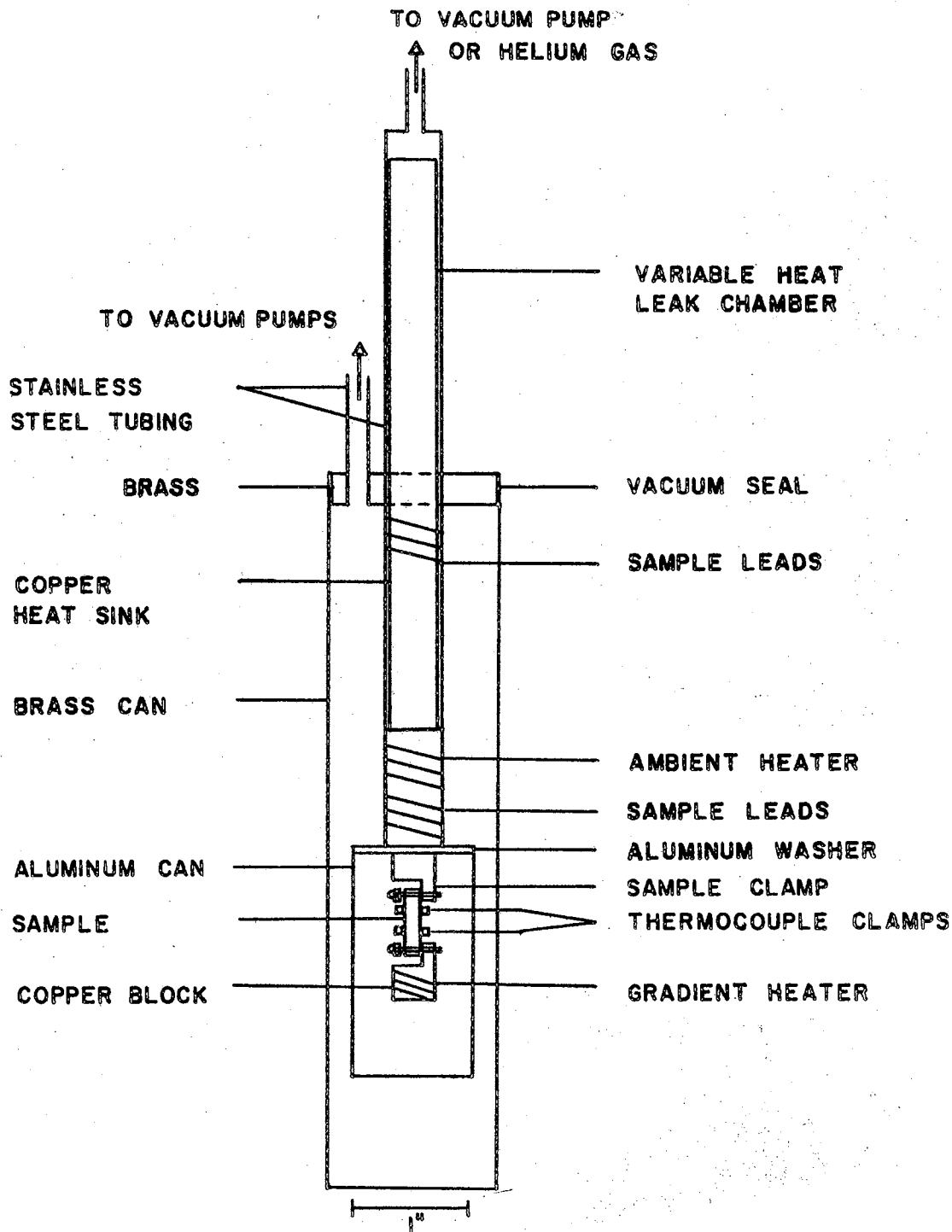


Figure 1. Sample Holder

gen was used for temperatures greater than 50 K.

A temperature gradient was applied to the sample by a 100 ohm wire heater which was wound around a copper block. This copper block was clamped to the free end of the sample. Good thermal contact was assured between the sample and the clamps on the heat sink and copper block by tinning the clamp faces with soft indium solder.

The ambient temperature of the sample was controlled by a 100 ohm wire heater wound around the heat sink. An aluminum can around the sample shielded the sample and minimized effects due to radiation.

All thermocouple, heater, and resistivity leads were introduced into the vacuum system through Conax vacuum seals. All leads were thermally anchored to the heat sink with GE7031 varnish both above and below the ambient heater. Thus, heat loss from the gradient heater due to these leads was made small by keeping the temperature difference between the sample and the heat sink small. All leads were of high thermal resistance, but if any heat was lost due to these leads, it was from the ambient heater, not the gradient heater.

The small thermocouple clamps shown in Figure 2 were placed on the sample and separated by some distance L . Resistivity and thermocouple leads were soldered to these clamps with indium solder. All electrical resistivity, heater, and copper thermocouple leads were of 40 gauge copper wire. The constantan and Au + .03 at. % Fe thermocouple wires were 36 gauge.

For temperatures less than 50 K the Au + .03 at. % Fe versus copper thermocouple was used. One of the thermocouple clamps had a sheet of teflon insulation between two copper plates. This made it possible to

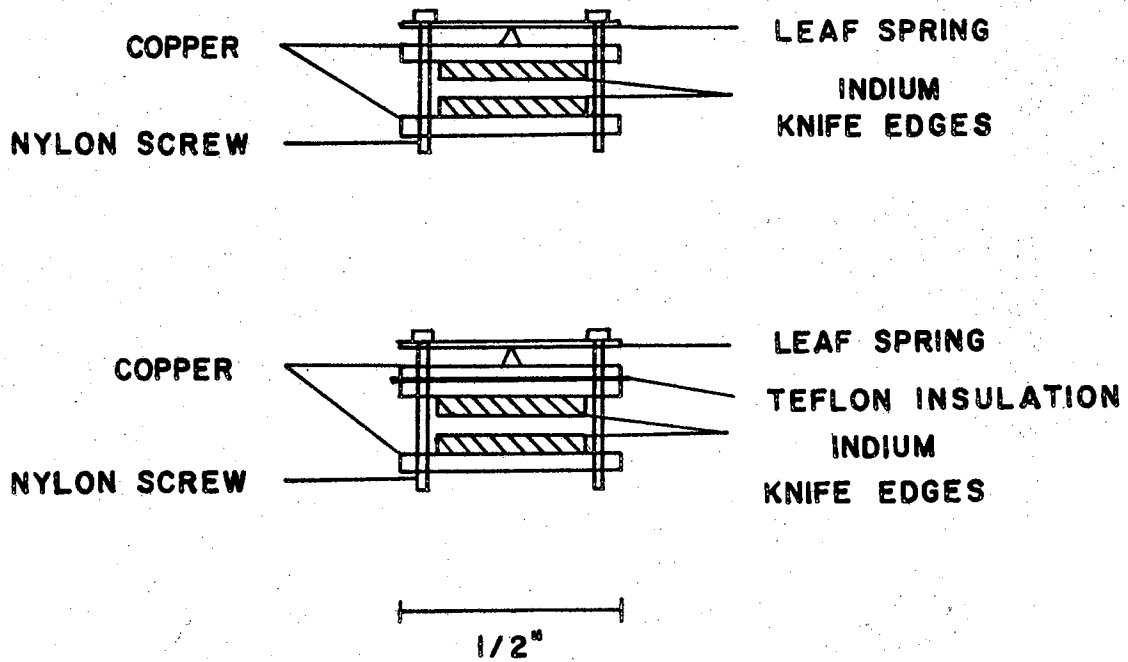


Figure 2. Thermocouple Clamps

measure the temperature difference between the two clamps with a differential thermocouple. For temperatures from 50-300 K copper versus constantan thermocouples were used. An ice bath was used as the reference temperature for both thermocouples. The Au + 0.03 at. % Fe wire was from a spool that had been calibrated at Iowa State University.

All voltages below 2 millivolts were measured with a Honeywell Model 2779 Potentiometer. Higher voltages were measured with a Leeds and Northrup K-3 Potentiometer. Power sources for the heaters were batteries.

Experimental Procedure

The samples measured in this work were obtained from Iowa State University. They were grown by electrolysis¹³ and annealed at 700-800 K until homogeneous. The samples were rectangular parallelepipeds with approximate dimensions of 15 mm. by 3 mm. by 3 mm. The criteria for homogeneity of the samples were that their electrical resistivity be uniform throughout the sample and that the room temperature resistivity obtained correspond to that measured by Muhlestein and Danielson² for that particular x-value. The resistivities cited in Table I differ from Muhlestein's values by no more than 7%.

The x-value of each sample was measured independent of this work²¹. The lattice constants were found by the x-ray powder method, and equation (1) of Chapter I was used to find the x-value. The lattice constants ranged from $a(\text{Å}) = 3.827$ at $x = 0.510$ to $a(\text{Å}) = 3.855$ at $x = 0.859$.

The electrical resistivity of all samples was measured at room tem-

perature (297 K) by a standard 4-point probe technique, which was independent of the sample holder. The samples were cleaned with a boiling solution of sodium hydroxide and water, and pointed tungsten electrodes were used on the cleaned surfaces.

Since the electrical resistivity is known independent of the sample holder at room temperature, it is possible to determine the geometrical factor, L/A , from the room temperature electrical resistance between the thermocouple clamps. It is important that the electrical resistivity and thermal conductivity be determined in the same apparatus. In determining the Lorenz ratio all error that may occur in this geometrical factor will divide out.

In measuring the thermal conductivity at some temperature controlled by the ambient heater, one must measure the power input to the gradient heater and the resultant steady-state temperature difference between the thermocouple clamps. It is assumed that all power supplied to the gradient heater must flow through the sample to the heat sink. The power needed for equation (3) is then

$$W = VI \quad (8)$$

where V is the voltage across the heater and I is the current through it. The temperature difference, $T_1 - T_2$, determined with the thermocouples then allows the thermal conductivity to be calculated. The magnitude of $T_1 - T_2$ is generally between 1 and 2 K for temperatures greater than 50 K. At 5 K, $T_1 - T_2$ is about .03 K.

The electrical resistivity was found by measuring the voltage drop between the thermocouple clamps when a known electric current was passed through the sample. The electrical resistivity, ρ , is given by

$$\rho = A/L \cdot V/I. \quad (9)$$

Experimental Results

The thermal conductivity and electrical resistivity of four sodium tungsten bronzes were measured over the temperature range 5-300 K.

Table I shows the x-value, room temperature electrical resistivity, residual resistivity, room temperature Lorenz ratio, and room temperature thermal conductivity of each sample. The Lorenz ratio was found from equation (5).

TABLE I
SAMPLE CHARACTERISTICS

x	ρ_{300} (10^{-6} ohm-cm)	$\rho_{res.}$ (10^{-6} ohm-cm)	λ (W/cm-K)	L (10^{-8} V ² /K ²)
0.859	16.8	3.92	0.463	2.76
0.754	21.1	7.61	0.403	2.88
0.700	27.6	10.9	0.321	3.05
0.510	54.8	30.5	0.219	4.05

Figure 3 shows the measured thermal conductivity of each sample. These values agree with the measurements made by Martin and Shanks¹ on intermediate x-values. Figure 4 shows the electrical resistivity of each sample.

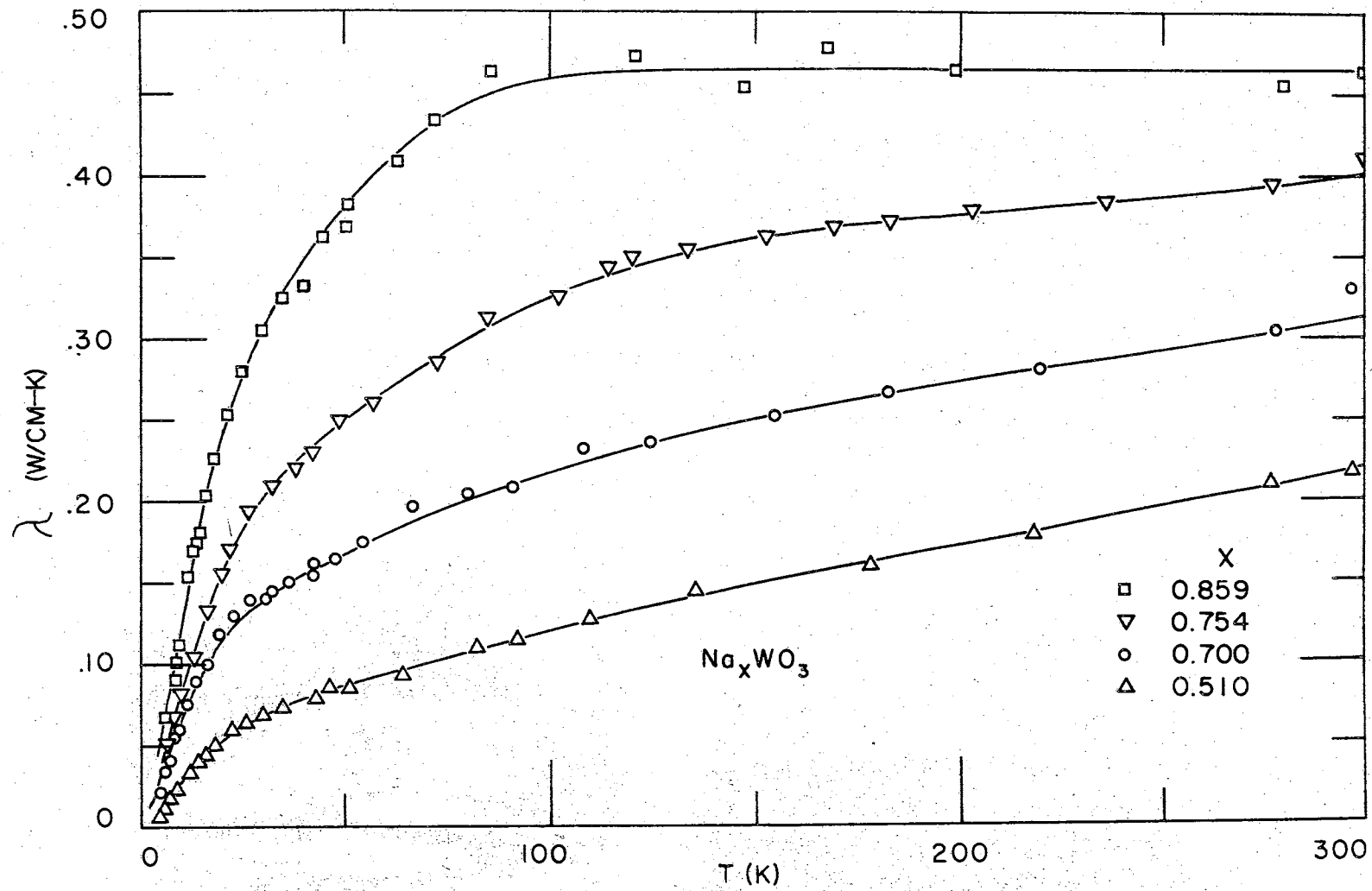


Figure 3. Thermal Conductivities Versus Temperature for the Four Samples

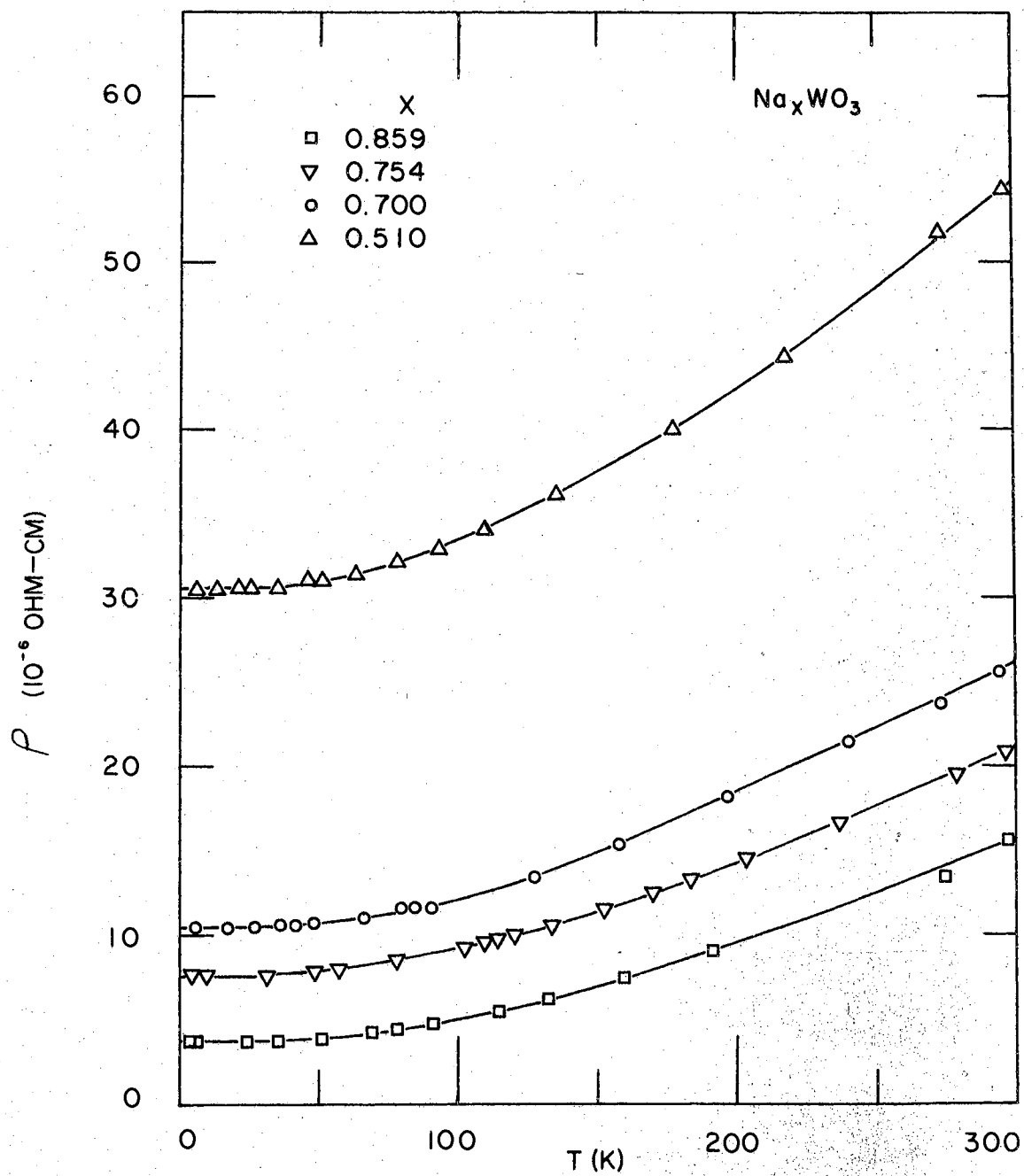


Figure 4. Electrical Resistivities Versus Temperature for the Four Samples

CHAPTER III

DISCUSSION OF RESULTS

Thermal Conductivity Results

The electrical resistivity data shown in Figure 4 compares well with measurements made by Muhlestein and Danielson². It can be seen that the residual resistivities are quite large, giving resistivity ratios that would correspond to low purity metals or alloys. The small resistivity ratios, however, do not mean that the samples are impure. A small resistivity ratio is an intrinsic property of Na_xWO_3 . The residual resistivity decreases with increasing x , indicating that the electron scattering by sodium vacancies is dominant in limiting the electrical resistivity.

The thermal conductivity, shown in Figure 3, increases with increasing x , which would suggest that the sodium vacancies play a major role in the scattering of phonons and electrons. The thermal conductivity appears to be linear with temperature for temperatures less than 20 K. This would indicate that the electronic component is dominant as in metals. In metals the electronic thermal conductivity is given by the Wiedemann-Franz Law,

$$\lambda = L_0 \sigma T \quad (1)$$

Since σ is constant for T less than 20 K, λ is linear with T . However, as will be shown later, a lattice component can be separated from this

total thermal conductivity that is as much as 50% of the total in this temperature range.

The thermal conductivity of the $x = 0.510$ sample agrees with the high temperature measurements on an $x = 0.513$ sample by Shanks and Redin¹⁷. They found the thermal conductivity to increase with temperature from 300-700 K. Shanks and Redin also measured the thermal conductivity of a sample with $x = 0.804$. The thermal conductivity of this sample increased very little with temperature. This temperature dependence corresponds with that of the higher x samples in this work. However, their thermal conductivity was less than the thermal conductivity of the higher x samples in this work.

At temperatures greater than 100 K the thermal conductivity is constant for the $x = 0.859$ sample, while it is linear with temperature for the other three samples. In comparing with the samples measured by Martin and Shanks¹, it should be noted that those samples with x less than 0.75 exhibit the linear temperature dependence, while those with x greater than 0.75 exhibit no temperature dependence in this temperature range. This is probably due to the ordering which occurs at $x = 0.75$.

Lorenz Ratio

The apparent Lorenz ratio calculated from equation (5) of Chapter II is shown in Figure 5. As was observed by Martin and Shanks¹, the Lorenz ratio reaches a maximum at 10 K and appears to decrease to the theoretical value, L_0 , as T approaches zero. At low temperatures electron-phonon interaction and sodium vacancy scattering should be the dominant mechanisms in limiting the lattice thermal conductivity. Accord-

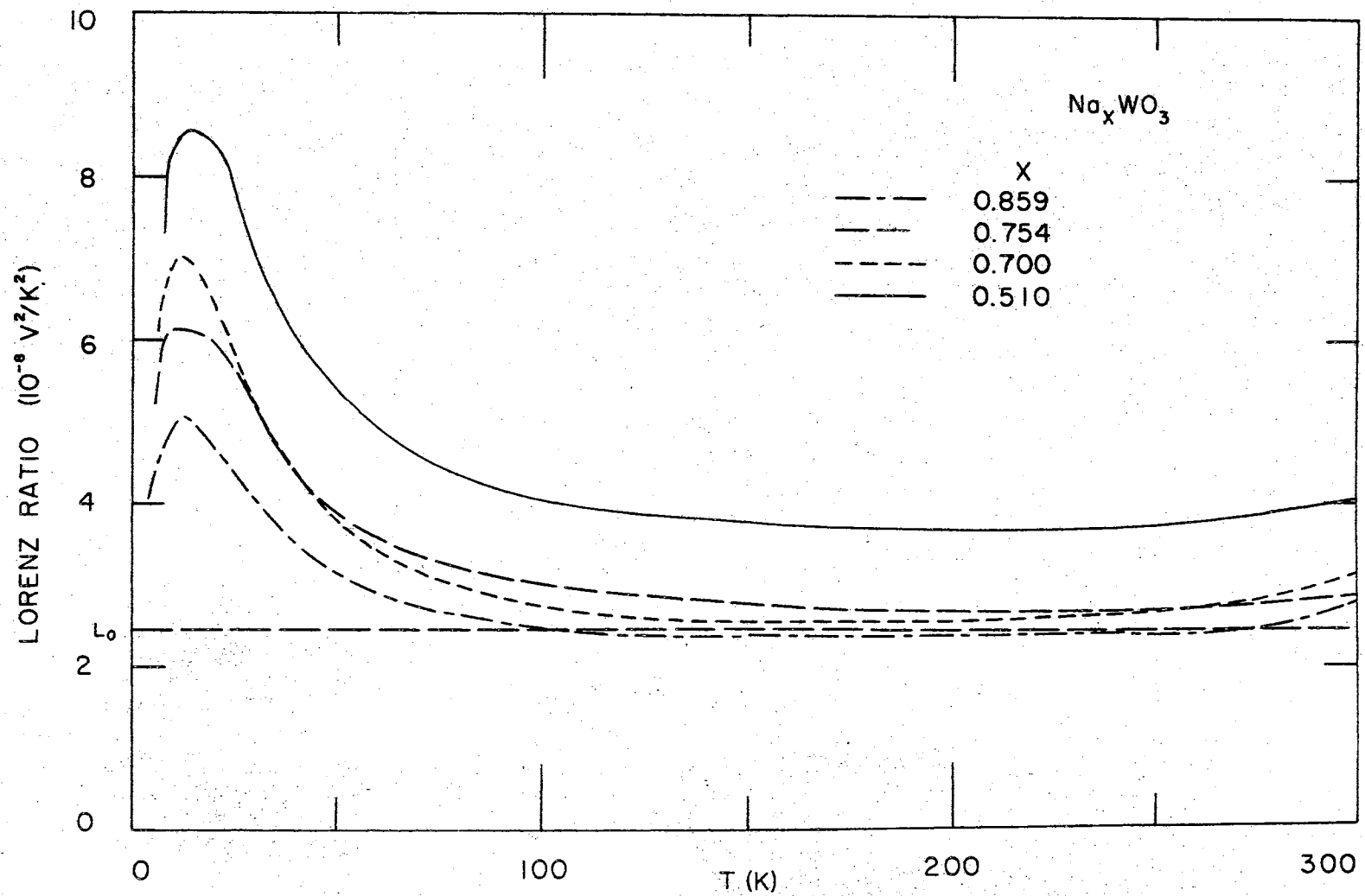


Figure 5. Apparent Lorenz Ratios Versus Temperature for the Four Samples

ing to Klemens¹⁹ the lattice thermal resistivity would be

$$1/\lambda_L = AT^{-2} + BT \quad (2)$$

where A and B are constants. AT^{-2} is the electron-phonon interaction term, and BT is due to sodium vacancy scattering. The lattice thermal conductivity is then

$$\lambda_L = T^2/A+BT^3. \quad (3)$$

The total thermal conductivity, λ , can then be represented by

$$\lambda = L_0\sigma T + T^2/A+BT^3, \quad (4)$$

where $L_0\sigma T$ is the theoretical electronic component. The apparent Lorenz ratio, L_m , will then be

$$L_m = \lambda/\sigma T = L_0 + T/(A+BT^3)\sigma. \quad (5)$$

In the limit as T approaches zero the apparent Lorenz ratio approaches the theoretical value since σ is constant at low temperatures.

If heat conduction by lattice vibrations is comparable with that due to electrons, the temperature dependence of the apparent Lorenz ratio will depend on which phonon scattering mechanism is dominant. If electron-phonon interaction is dominant, L_m will be linear with T . For temperatures less than 10 K it appears that this mechanism is dominant. If sodium vacancy scattering is dominant, L_m will have a term in T^{-2} . Phonon-phonon interaction will also add a term to the thermal resistance approximately linear with temperature. For the temperature range 10-120 K it would appear that a combination of sodium vacancy scattering and phonon-phonon interaction limits the lattice conductivity. Above 120 K the lattice conductivity should be small compared with the electronic component.

The sharp peak in the apparent Lorenz ratio at 10 K is opposite to

that seen in most pure metals. Since the electrical resistivity is constant throughout this temperature range, this maximum must be attributed to the thermal conductivity. Estermann and Zimmerman²² observed Lorenz ratios several times greater than the theoretical value for several metallic alloys at these temperatures. They attributed the large maximum in the Lorenz ratio to be due to lattice conduction. The temperature range of the maximum is the same temperature range in which Martin and Shanks¹ observed lattice conduction for their $x = 0.862$ sample. These maxima in the Lorenz ratio will, therefore, be attributed to lattice conduction.

For the temperature range 120-220 K the apparent Lorenz ratio is constant. The increase in L above 220 K is probably due to radiation losses from the gradient heater, and is not characteristic of Na_xWO_3 . All further statements will, therefore, refer to data below 220 K. The constant Lorenz ratio is very near the theoretical value for the three higher x samples, but is much higher for $x = 0.510$. Martin and Shanks also observed that the apparent Lorenz ratio was higher than the theoretical value at these temperatures for small x and approached L_0 as x increased.

Lattice Component of Thermal Conductivity

In estimating a lattice component for the thermal conductivity, Martin and Shanks assumed the electronic component to be $L_0\sigma T$ and subtracted this value from the measured thermal conductivity at T to determine the lattice component. Their lattice thermal conductivity for all samples except $x = 0.862$ was large and temperature independent at high

temperatures. It can be seen that since the apparent Lorenz ratios in this work are larger than L_0 ,

$$\lambda_L = \lambda - L_0 \sigma T, \quad (6)$$

would be large at high temperatures for these samples, also. The calculated lattice component for the $x = 0.862$ sample had a maximum at 25 K and decreased with temperature at high temperatures. The temperature dependence was what one would expect for phonon-phonon interaction.

Table II gives the room temperature electrical resistivities, thermal conductivities, and Lorenz ratios of the samples measured by Martin and Shanks. In order to better observe the way Na_xWO_3 depends on x , all further Figures and Tables will include their samples. The x -values of their $x = 0.64$ and $x = 0.89$ samples were checked at the same time as the samples for this work. They were found to actually have x -values of 0.628 and 0.862, respectively. Their $x = 0.51$ sample was not measured for T less than 50 K. The $x = 0.510$ sample in this work was cut from the same ingot as their sample.

TABLE II
SAMPLES MEASURED BY MARTIN AND SHANKS

x	ρ (10^{-6} ohm-cm)	λ (W/cm-K)	L (10^{-8} V^2/K^2)
0.89 (0.862)	15.4	0.53	2.7
0.78	22.0	0.53	3.8
0.64 (0.628)	37.0	0.30	3.5
0.51	48.0	0.22	3.5

In order to estimate the lattice component of the thermal conduct-

ivity, it was assumed that the constant apparent Lorenz ratio in the temperature range 120-220 K was the intrinsic value for each sample. That is, it was assumed each x-value had a particular Lorenz ratio, L_x . A Lorenz ratio larger than the theoretical value is common in transition metals such as thorium²³, titanium, and hafnium²⁴. The large Lorenz ratio for thorium was attributed to deviations from the free electron model, and was related to the band structure of thorium. Muhlestein and Danielson² concluded from their Hall coefficient measurements, that the electronic properties of Na_xWO_3 could not be explained by a free-electron approximation. Greiner, et al.²⁵ found the slope of the measured magnetic susceptibility versus x curve to be greater than that given by a nearly free electron calculation. They concluded that a nearly free electron model was not satisfactory in describing Na_xWO_3 . Since the lattice component of the thermal conductivity should decrease with temperature, the large value for the Lorenz ratio is not caused by lattice conduction. Therefore, it has been concluded that the actual Lorenz ratios for the samples are larger than L_0 at high temperatures. Table III shows the assumed Lorenz ratio for each sample. The large Lorenz ratios for the low x samples correspond to those of metals and alloys with relatively low electrical conductivity. Thus, Na_xWO_3 has the transport properties of a high conductivity metal for large x and a low conductivity metal for small x. The large value of L_x for x = 0.78 will be discussed later.

The lattice component of the thermal conductivity was calculated by assuming the electronic component to be

$$\lambda_x = L_x T / \rho. \quad (7)$$

The lattice component is then given by

$$\lambda_L = \lambda - \lambda_x, \quad (8)$$

where λ is the measured thermal conductivity. It should be noted that the Lorenz ratio, L_x , is assumed constant for all temperatures when in fact it approaches L_0 at low temperatures. Since the temperature range over which L_x approaches L_0 is the same temperature range in which λ_L is observable, this assumption must be used.

TABLE III

ASSUMED LORENZ RATIOS

x	L_x ($10^{-8} \text{ V}^2/\text{K}^2$)
0.510	3.70
0.628	3.10
0.700	2.60
0.754	2.69
0.78	3.60
0.859	2.38
0.862	2.46

The estimated lattice component is shown in Figure 6 for each sample listed in Table III. It can be seen that the lattice component for each sample has a maximum at about 25 K. Since these maxima increase with x, sodium vacancy scattering is dominant in limiting the lattice component above this temperature. This agrees with the conclusions made concerning the Lorenz ratio. The $x = 0.754$ sample has a peak

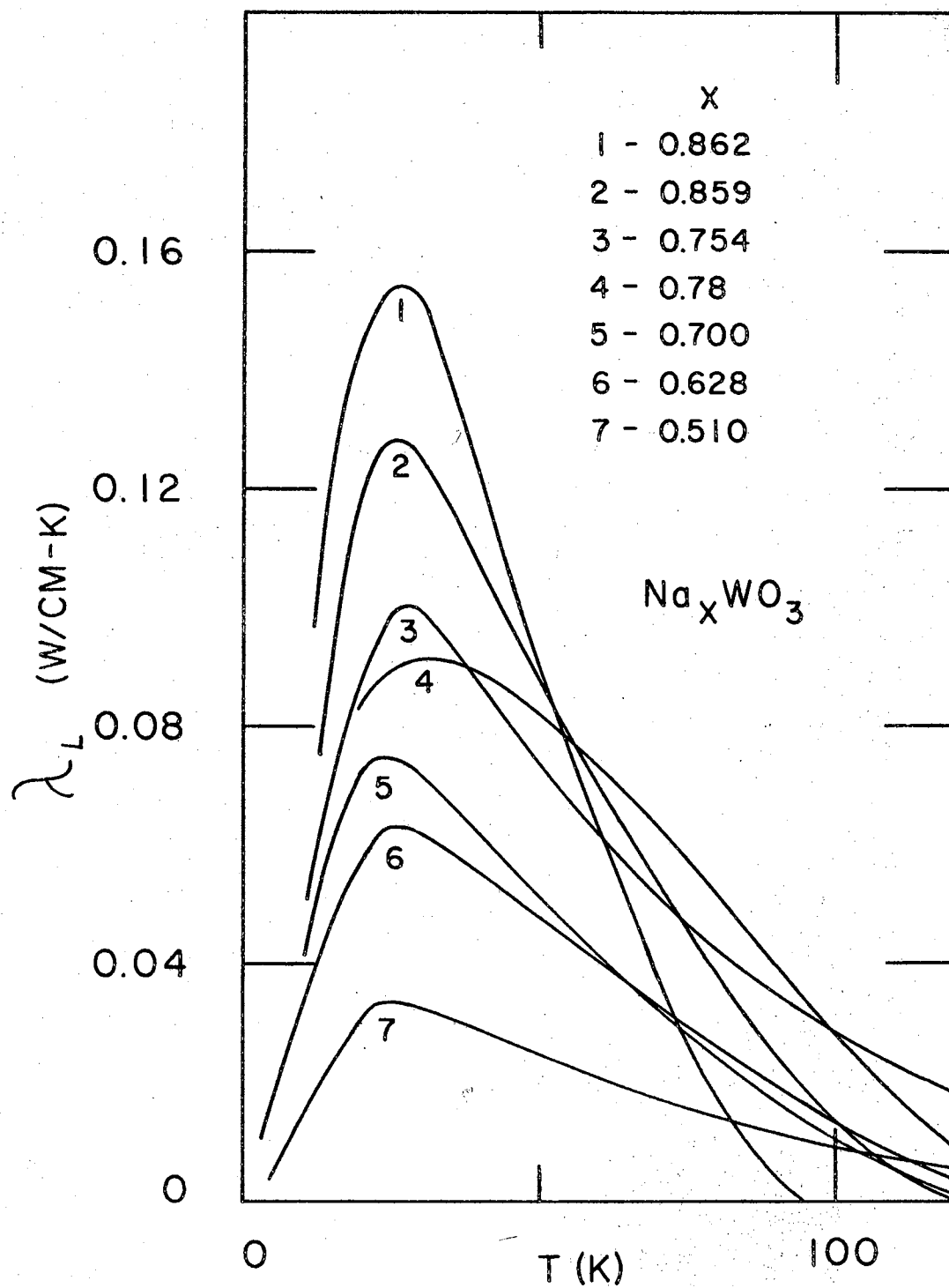


Figure 6. Estimated Lattice Component of the Thermal Conductivity

slightly greater than the $x = 0.78$ sample. This is probably due to the uncertainty in determining L_x . For T less than 30 K this estimated lattice component is approximately 50% of the total thermal conductivity.

If electron-phonon interaction were dominant, the lattice component would decrease with increasing x since the electron concentration, and thus scattering probability increase with x . Electron-phonon interaction must, therefore, be significant only at very low temperatures. The lattice component appears to be proportional to some power of T between one and two at low temperatures. This indicates that λ_L is limited by a combination of electron-phonon interaction and sodium vacancy scattering.

At temperatures higher than 25 K the lattice component should be limited by a combination of phonon-phonon interaction and sodium vacancy scattering. According to Klemens¹⁹ for temperatures less than the Debye temperature, θ , the temperature variation of the thermal resistivity for phonon-phonon interaction is

$$1/\lambda_L = DT^{-3} e^{-\theta/bT}, \quad (9)$$

where b and D are constants. If thermal resistivities are assumed to be additive, then

$$1/\lambda_L = CT + DT^{-3} e^{-\theta/bT} \quad (10)$$

for a combination of sodium vacancy and phonon-phonon scattering where C is a constant. The thermal conductivity would then be

$$\lambda_L = T^3 / (CT^4 + De^{-\theta/bT}). \quad (11)$$

Phonon-phonon interaction is important only at higher temperatures while sodium vacancy scattering should be important at all temperatures. Thus, at 25 K sodium vacancy scattering is probably dominant while at

higher temperatures the two mechanisms should be comparable. From equation (11), λ_L should be proportional to T^{-1} for temperatures near 25 K while at higher temperatures phonon-phonon interaction increases the denominator so that λ_L is damped faster than T^{-1} .

Since the lattice constants of Na_xWO_3 change very little with x , the phonon-phonon interaction should be nearly independent of x . The mechanism that makes λ_L a function of x should, therefore, be sodium vacancy scattering. Sodium vacancy scattering appears to be as important in limiting the thermal conductivity as it is in limiting the electrical conductivity.

Anomalous Behavior of Thermal Conductivity

Muhlestein and Danielson² observed an inflection point in the resistivity versus x -value curve at $x = 0.75$. Figure 7 shows the thermal conductivity plotted as a function of x for several temperatures. The electrical conductivity data of Muhlestein and Danielson is included for comparison. The thermal conductivity is a smoothly varying function of the sodium concentration for x less than 0.78. An anomaly similar to that observed in the electrical conductivity occurs between $x = 0.78$ and 0.859. The anomaly is shown in Figure 7 to occur at $x = 0.78$. More samples with intermediate x -values must be measured to determine the actual position of the inflection point.

The discovery that anomalous behavior occurs at some value of x greater than 0.75 rather than at 0.75 was not expected. The validity of the measurements on the $x = 0.78$ sample were first of all questioned. However, the thermal conductivity of this sample has been checked on the

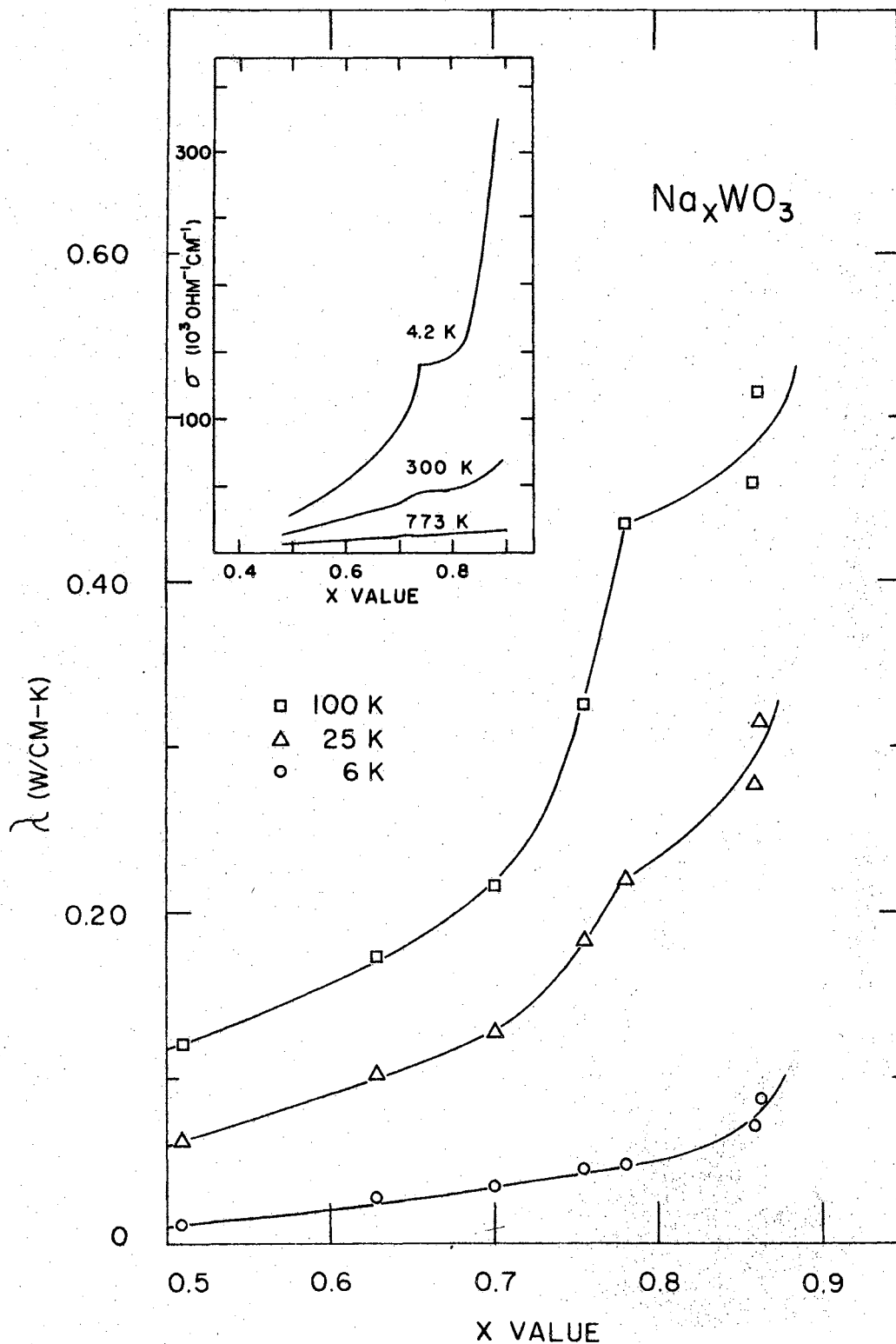


Figure 7. Thermal Conductivity as a Function of x for Several Temperatures. The Inset Gives the Electrical Conductivity Data of Muhlestein and Danielson

apparatus used in this work. These measurements were found to be in excellent agreement with the original data.

Since the estimated lattice component shows no anomaly at $x = 0.75$, the anomalous behavior must be related to the band structure of Na_xWO_3 . According to Goodenough¹³ there are two types of carriers present for x greater than 0.75. He also suggests, however, that the number of electrons in the first conduction band decreases roughly as $(6-7x)$. Thus, for x greater than 0.86 conduction will be primarily by one type of carrier. The anomalous behavior occurs at some value of x between 0.78 and 0.859, rather than at 0.75, due to the large deviation in the Lorenz ratio for samples in this range. Figure 8 shows the ratio L_x/L_0 plotted versus x . For x less than 0.75 this ratio approaches one. At $x = 0.75$ this ratio begins to increase so that a maximum occurs near $x = 0.78$. The ratio then decreases to the theoretical value at $x = 0.86$. For x between 0.75 and 0.86 there is conduction by two slightly overlapping energy bands. According to Price²⁶ large deviations in the Wiedemann-Franz Law will occur for two overlapping energy bands. This would explain qualitatively the large Lorenz ratio for this range of x .

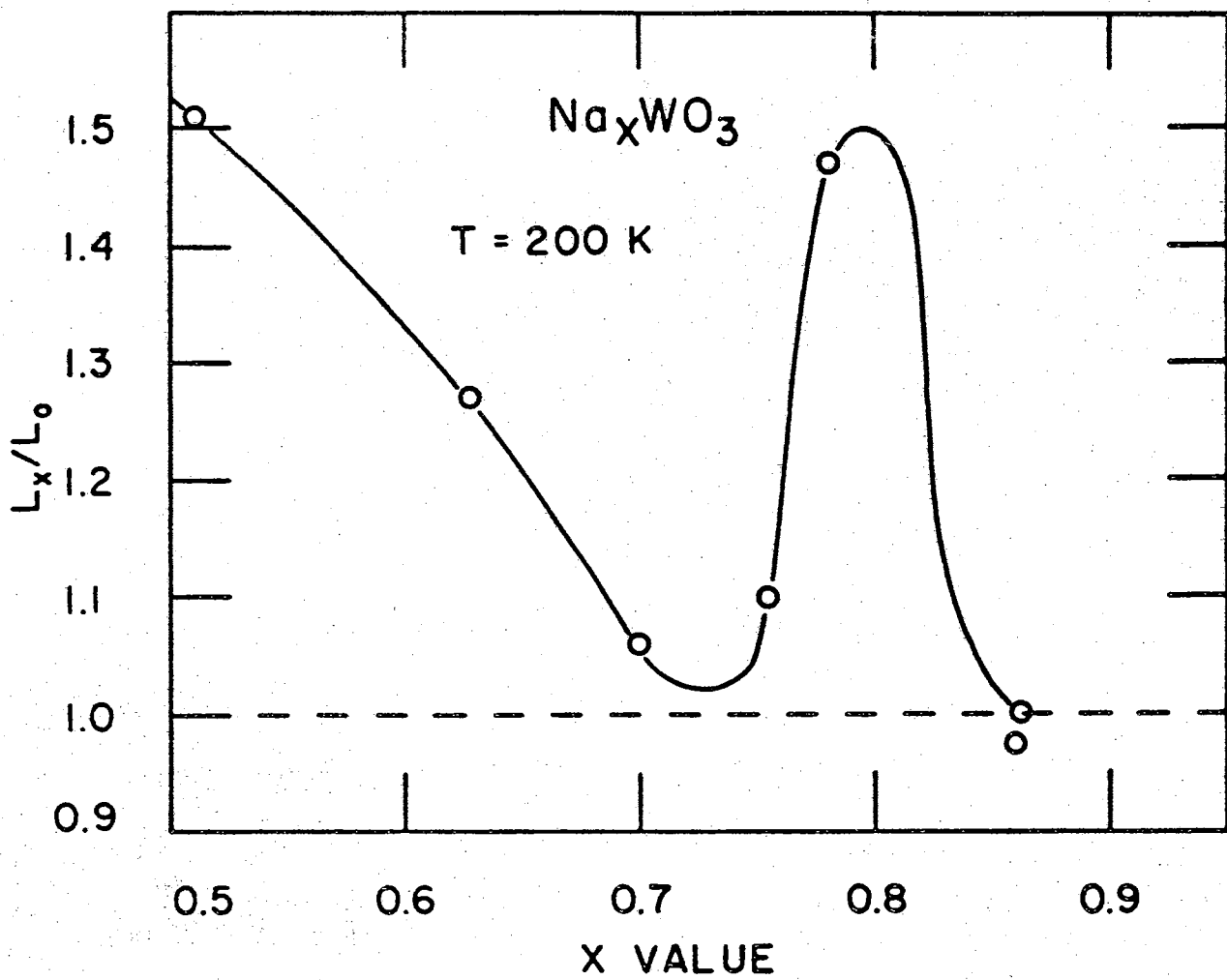


Figure 8. Ratio of the Assumed Lorenz Ratio to the Theoretical Value as a Function of x

CHAPTER IV

SUMMARY

The thermal conductivity and electrical resistivity of four sodium tungsten bronzes, Na_xWO_3 , have been measured over the temperature range 5-300 K. The x-values of the samples ranged from 0.510 to 0.859. A steady-state heat flow apparatus was used for measuring the thermal conductivity. The electrical resistivity was measured in the same apparatus so that the geometrical factor, L/A , was the same for both the thermal conductivity and the electrical resistivity.

The thermal conductivity was found to increase with increasing x. Since each sodium atom contributes one conduction electron, the conduction electron concentration increases with x, while the number of sodium vacancies decreases with x. This would indicate that sodium vacancy scattering rather than electron-phonon interaction is dominant in limiting the thermal conductivity.

For temperatures above 120 K the apparent Lorenz ratio was constant for all samples. This constant Lorenz ratio was larger than the theoretical value, L_0 , for small x, and approached L_0 as x increases. A maximum in the apparent Lorenz ratio was observed at 10 K for all samples. This maximum was attributed to significant lattice conduction at low temperatures.

If the electronic component of the thermal conductivity is assumed

to be $L_0\sigma T$, then the resulting lattice component is large and nearly constant at high temperatures. However, the lattice component should be limited by a combination of sodium vacancy and phonon-phonon scattering at high temperatures. By assuming the constant high temperature Lorenz ratio, L_x , to be the intrinsic value for each sample, a lattice component of the thermal conductivity, λ_L , was obtained. The lattice component was given by

$$\lambda_L = \lambda - L_x T / \rho \quad (1)$$

where λ is the measured thermal conductivity, and ρ is the extrapolated electrical resistivity at the temperature, T . This procedure was also applied to the samples of Martin and Shanks¹. A maximum in the lattice component was observed at 25 K for each sample. The estimated lattice conductivity appeared to be limited by sodium vacancy scattering at all temperatures. At temperatures less than 10 K electron-phonon interaction should be significant. Phonon-phonon interaction appeared to be large at temperatures above 25 K.

The thermal conductivity of the samples measured and the samples of Martin and Shanks was plotted as a function of sodium concentration, (x). An anomalous behavior similar to that observed by Muhlestein and Danielson² for the electrical conductivity was observed at $x = 0.78$. This anomalous behavior was attributed to ordering of the sodium atoms at $x = 0.75$ and the formation of a superlattice. According to Goodenough¹³ for x between 0.75 and 0.86 there are two types of carriers present. In this range of x large deviations from the Wiedemann-Franz Law could occur. For the $x = 0.78$ sample of Martin and Shanks the apparent Lorenz ratio at high temperatures was $3.6 \times 10^{-8} \text{ V}^2/\text{K}^2$. For $x = 0.754$ and

0.859 the apparent high temperature Lorenz ratios were near the theoretical value.

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