Heat Capacities, Magnetic Properties, and Resistivities of Ternary RPdBi

Alloys where R = La, Nd, Gd, Dy, Er, and Lu

by

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1. INTRODUCTION

1.1. Rationale

Over the past four and a half decades research on the rare earths, their compounds, and their alloys has yielded significant insights into the nature of materials (1). The rare earths can be used to systematically study a series of alloys or compounds (2). Magnetic ordering, crystalline fields, spin fluctuations, the magnetocaloric effect, and magnetostriction are a small sample of phenomena studied that are exhibited by the rare earth family.

A significant portion of research has been conducted on the abundant RM_2 and RM phases, where R is the rare earth and M is a transition metal. The natural progression of science has led to the study of related RMX ternary phases, where X is either another transition metal or semimetal. There are now over 1000 known RMX phases (3). The focus of this study is on $RPdBi$ where $R = La, Nd, Gd, Dy, Er, \text{ and } Lu$. $RPdBi$ crystallizes with the $AlLiSi$ structure type ($cF12 F\bar{4}3m$ space group), though often referred to as $AgAsMg$ in much of the literature. This structure has been described as the "rock salt plus one," i.e. essentially three face centered cubic sublattices located at $(0,0,0)$, $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$, and $(\frac{3}{4}, \frac{3}{4}, \frac{3}{4})$ along the body diagonal. With the sublattices being $Pd, R, \text{ and } Bi$, respectively (4,5).

1.2. Lanthanides

The electron configuration of neutral isolated lanthanide atoms is generalized as: $[\text{Xe}]5d^1 4f^n 6s^2$. Where $[\text{Xe}]$ is the closed shell configuration of Xenon and n ranges from 0 for lanthanum to 14 for lutetium. The 4f shell lies below the $5d^1 6s^2$ shells, these s and d shells interact with the electron clouds of neighboring atoms and thusly the lanthanides generally carry a valence of 3 conduction electrons.

One consequence of this configuration is the lanthanide contraction (6). The radius of the 4f shell decreases with the number of electrons added, i.e. as the atomic number increases. With an effective screening less than unity per additional electron the nuclear charge seen by the 4f shell increases progressively causing the 4f shell to contract. Physically this is detected by the smaller lattice constants in an isostructural series of lanthanide compounds as the atomic number of the lanthanide increases. With the exceptions of cerium, samarium, europium, and ytterbium, the pure lanthanides crystallize with an dhcp (La, Nd, Pr, and Pm) or hcp structure.

Magnetic phenomena occurring in lanthanide containing compounds arises from unpaired 4f electrons (7). Hence, all the lanthanides order magnetically except for the end members,

lanthanum and lutetium. The effective moment is calculated from

$$P_{eff} = g\sqrt{J(J+1)} (\mu_B) \quad (1)$$

where J is the total angular momentum, which originates from the coupling of the spin and orbital momentum. The electron spins couple to give the total spin, S , and the 4f electron's orbital angular momentum couple to give the total orbital momentum, L . The light lanthanides S and L couple for a total angular momentum of $L+S$. The coupling for the heavy lanthanides produces J equal to $L+S$, with the angular momentum in the ground state having $2J+1$ associated quantum states.

The $2J+1$ degenerate states in J are split by the magnetic interactions of the 4f ions via an exchange magnetic field and/or a crystalline electric field (8). The entropy, ΔS , available for magnetic interactions is calculated by

$$\Delta S = R \ln(2J+1) \quad (2)$$

where R is the gas constant. The substantial entropy available as the metals pass from magnetic to a nonmagnetic state (and vice versa) is physically exhibited as a large anomaly in the heat capacity.

2. EXPERIMENTAL METHODS

2.1. Sample Preparation and Characterization

The samples used in this study were prepared by sealing stoichiometric portions of high purity constituents in a tantalum crucible, under an inert helium atmosphere, and melting in an induction furnace. A graphite insulated receptor can was centered in the induction coils with the sample centered in the can and surrounded by several extra receptors. A tungsten-rhenium thermocouple was used to monitor the temperature. Each sample was melted three times at $\sim 1500^{\circ}\text{C}$, and allowed to radiatively cool to room temperature under vacuum. The Ta crucible was inverted after each melt to ensure homogeneous mixing. Next, the Ta crucibles were individually sealed in quartz tubes and initially heat treated for one week.

The lanthanide elements were prepared by the Materials Preparation Center, Ames Laboratory, DOE. Results from laser source mass spectroscopy (LSMS), or spark source mass spectroscopy (SSMS), and vacuum fusion (VF) analysis for each is listed in Table 1. The bismuth was produced by Cominco and taken from Lot EM4422. Cominco lists the Bi as 6-9's pure. Palladium was produced by Engelhard, lot Pd-AGA-37, chemical analysis for Pd is also reported in Table 1.

Table 1. Chemical Analysis of Starting Materials (only impurity levels <1 ppm atomic are listed).

Impurity	La"	Nd"	Gd*	Dy"	Er*	Lu*	Pd'
H	690	-	622	800	-	346	-
C	345	48	301	10	97	189	(4.6)
N	110	103	314	46	48	37	(3.7)
O	510	478	933	500	640	130	(860)
F	29	<3	<3	81	98	<3	-
Na	-	-	-	-	-	-	1
Mg	-	-	-	-	-	-	13
Al	11	5	1	4.2	2	5	3
Si	16	29	10	7.5	-	-	37
P	-	-	3	-	-	-	1.2
S	1	-	-	-	-	-	-
Cl	10	3	6	23	4	5	6.3
K	-	-	-	-	-	-	1.6
Ca	-	-	-	-	1.8	-	14
Sc	-	-	-	<2	-	<2	-
Ti	-	4	-	-	-	-	36
Cr	-	18	3	3	1	1	<2
Mn	-	2.8	-	24	11	-	-
Fe	5	50	7	81	2.9	25	13
Ni	-	1.5	22	-	2	-	-
Cu	2.2	3.6	3.7	-	3.6	2	2.2
As	-	<10	-	-	-	-	-
Br	-	-	-	<300	-	-	-
Y	3	2	9	9	-	1	-
Nd	-	-	-	-	-	2	-
Mo	-	-	-	-	6	-	-
Rh	-	-	-	-	-	-	<5
Sn	-	-	-	-	-	-	2.2
Ba	1	-	-	-	-	-	-
La	-	-	5.8	-	-	<3	-
Ce	1	-	10	-	-	-	-
Pr	-	1.7	4	-	-	-	-
Nd	-	-	-	<2	-	-	-
Sm	-	-	-	<2	-	-	-
Gd	-	-	-	<3	-	-	-
Tb	-	-	14	-	-	1	-
Dy	-	-	-	-	<3	-	-
Ho	-	-	-	<7	8.8	-	-
Hf	-	-	-	<2	-	-	-
Ta	-	7	3	17	6	-	-
W	-	-	-	-	<4	5.6	-
Pt	-	-	-	-	-	-	10
Au	-	-	-	<2	-	-	-
Pb	-	-	-	-	3.8	-	-

Methods: "LSMS and VF, *SSMS and VF, 'LSMS (see text for definitions of acronyms).

The samples were removed from their crucibles by machining the Ta off with a lathe. Each was examined by x-ray diffraction and metallographically for homogeneity, while LaPdBi was also examined with scanning electron microscopy. Table 2 lists the heat treatment temperatures that produced single phased materials.

Table 2. Heat Treatment Schedule for RPdBi samples.

RPdBi	HT Temp. (°C)	Duration	Homogeneous
La	925	1 Week	See Text
Nd	1200	1 Week	Yes
Gd	1000	1 Week	Yes
Dy	900	9 Days	Yes
Er	1000	1 Week	See Text
Lu	1100	1 Week	Yes

Diffraction analysis was performed with a SCINTAG PAD V diffractometer. Powder specimens were prepared by grinding a small piece of the sample with a mortar and pestle. A greased microscope slide was used to mount the powder on the rotating sample holder. The computer controlled diffractometer utilized Cu K α radiation with a graphite monochromator attached to the detector. A continuous scan over the 2 θ angular range of 20 to 90 degrees at a rate of 0.30 deg/min was used. Crystal Structure Determination, Release 94, was

used to calculate the lattice parameters using a least squares routine, and the theoretical densities were also calculated (9). Lattice parameters and densities for the RPdBi series appear in Table 3 below, along with the lattice constants reported in literature for RPdBi structures (4). The lattice parameter for ErPdBi was interpolated from values of HoPdBi and YbPdBi reported in the above citation.

Table 3. Lattice Parameters and Theoretical Densities

RPdBi	Measured a (Å)	Reported a (Å)	Density g/cm ³
La	6.8747(7)	-	9.2865(5)
Nd	6.7406(5)	6.778(2)	9.967(2)
Gd	6.6750(5)	6.698(2)	10.555(2)
Dy	6.6351(8)	6.643(2)	10.865(5)
Er	6.6031(5)	(6.6)	11.134(3)
Lu	6.5724(7)	-	11.471(5)

X-ray diffraction can only detect a second phase to a lower limit of ~5%. If extraneous diffraction maxima were present the sample was resealed in a Ta vessel and further annealed. If the pattern contained no extra peaks the sample was examined metallographically, which can detect the presence of extra phases with a lower limit of ~1%.

Metallographic samples were polished then etched in Nitol for 10 seconds. Only LaPdBi and ErPdBi showed the presence of

a second phase. ErPdBi contained $\leq 1\%$ second phase, subsequently, experimental measurements were conducted with the initial sample. About $\sim 5-8\%$ second phase in LaPdBi was present despite an x-ray diffraction pattern that contained no extraneous peaks above background levels. However, the diffraction pattern exhibited some "shouldering" on the peaks. Utilizing a scanning electron microscope with an energy dispersive x-ray diffraction(EDS) attachment, the composition of the second phase was examined. At a magnification of 1100x the grain of the second phase region was just perceivably brighter in appearance. An x-ray dot map of the sample surface was made for each element. No significant differences in elemental distribution could be seen. Further, an EDS spectrum was taken in both regions, the difference in intensity of the Bi peaks indicates a Bi-rich second phase, on the order of $\leq 5\%$ difference in Bi content. The apparent second phase is attributed to a Bi-rich(Pd-depleted) phase of LaPdBi. Despite this presence, experimental measurements were performed on this specimen.

2.2. Heat Capacity

Heat capacity measurements were taken over temperatures ranging for 1.5K to room temperature under magnetic fields of up to 10T. Two adiabatic heat pulse calorimeters were used,

one for the temperature region 1.5K to 30K, and one from 3.5K to room temperature (10,11). The large temperature overlap allows for accurate matching of the two curves.

Measurements were made on 1-3g of material either in bulk or powder compact form. The bulk samples were cut on a diamond saw to have two parallel surfaces of large diameter, and weighed to $\pm 0.0001\text{g}$ accuracy. A small, measured amount of grease is applied to both surfaces to ensure good thermal contact with the sample holder. Powder samples consisted of 2-3g of sample material ground to ~ 80 mesh to which is add 25% wt. silver powder (80-100 mesh). After thoroughly mixing the silver with the sample, the powders are compacted in a 1/4 inch diameter die under an applied load of 35,000 pounds. Similarly, grease is applied to the sample surface to ensure good thermal contact.

The two calorimeters have some common elements in their design:

- (1) Oil diffusion pumps backed by mechanical pumps provide the necessary vacuum conditions
- (2) Sample holders are attached to a liquid helium reservoir via a mechanical heat switch. Operating the switch will raise the temperature of the sample holder $\sim 0.1 - 0.3\text{K}$.
- (3) Vacuum pumping on the He reservoir lowers the temperature of the He/sample holder, to the He λ -

point or lower in the low temperature calorimeter, or to $\sim 3.5\text{K}$ in the high temperature unit.

- (4) The gold-plated copper sample holders are suspended within a cylindrical frame by nylon string. Each utilize a resistance heater and temperature sensors directly mounted to the sample holder. The complete unit is the addenda.

(a) A noninductively wound number 40 manganin wire resistance heater acts as the heat source and a germanium resistance thermometer (GRT) is used to monitor the temperature on the low temperature calorimeter.

(b) A strain gauge is used as the resistance heater and two temperature gauges are used. Carbon glass and platinum resistance thermometers are used. The carbon glass is calibrated to $\sim 40\text{K}$ and the platinum sensor is used from $\sim 40\text{K}$ to 350K .

The designs start to diverge past this point. The low temperature unit utilizes a nitrogen jacketed helium dewar that serves a dual purpose, cooling both the superconducting magnet and the sample space. The sample space is kept at high vacuum pressures but no further insulating of the sample is done, hence, as temperatures approach 30K the surrounding

chamber walls at 4.2K act as a heat sink. This factor limits the range of temperatures experimentally available.

The high-temperature calorimeter's super insulated helium dewar is dedicated to cooling the superconducting magnet, while a probe chamber is kept under high vacuum pressures. The probe contains the sample space, addenda, and helium reservoir. In addition to the vacuum insulation the sample is surrounded by an adiabatic heat shield(AHS). The AHS is used to maintain(attempts to maintain) a constant sample temperature either immediately before or immediately after the heat pulse. Utilization of the AHS allows the calorimeter to be operated at elevated temperatures.

Though physically different in design, both operate on the same principle. If a known amount of heat, ΔQ , is applied to a material, a corresponding temperature change defines the heat capacity:

$$C = \frac{\Delta Q}{\Delta T} \quad (3)$$

More rigorously this function is defined by differential elements δQ and δT . This relates to the calorimeter's operation in the following way:

A timed current pulse, I , is applied to a resistance heater generating a heat pulse. The total energy of the pulse, ΔQ , is found by integrating Joule's Law, $P=IV$, over the time of the pulse. The heat capacity, C , of the sample can now be found:

$$C_{\text{sample}} = \frac{\int IV dt}{\Delta T} - C_{\text{addenda}} \quad (4)$$

where ΔT is the temperature change resulting from the heat pulse. C_{addenda} is the heat capacity of the sample holder, grease, and silver powder if a powder compact was used. A calibrated addenda measurement is needed for each magnetic field used. The low temperature calorimeter calibration is described in reference (10). Information on the operation of the high temperature calorimeter can be found in reference (11).

2.3. Magnetic Measurements

A Lakeshore Model 7225 AC susceptometer/DC Magnetometer was used to measure AC and DC susceptibility and magnetizations. Operating temperatures range from 2.2K to room temperature for magnetic field up to 5T.

The system's main features are:

- (1) A liquid He cooled 5T superconducting magnet in a super insulated He dewar.
- (2) Sample probe consisting of a 0.25 inch stainless steel rod. The top of the probe is threaded and has a locking nut which attaches to a stepping motor atop the cryostat. The bottom ends in a threaded nylon rod. A few hundred milligrams of sample (powder

or bulk) material are enclosed in a nylon end cap which threads onto the nylon rod.

- (3) A molecular drag pump backed by a diaphragm pump provides the necessary vacuum conditions.
- (4) The sample probe is inserted into the cryostat which contains the sample heater, temperature sensors, and the pick-up coils.
- (5) Lakeshore ACS 7000 and DCM 7000 system software controls the drivers for the temperature controls, pick-up coils, stepping motor, and the magnet, from a personal computer.

The mass susceptibility, χ , of a sample is measured by moving the sample between the primary and secondary pick-up coils in the presence of a magnetic field. The translational motion of the sample creates a change in the magnetic flux. This flux change induces a voltage change in the sensing coils which is proportional to χ . The proportionality is written:

$$\chi = \frac{\alpha V_{rms}}{mfH_{rms}} \quad (5)$$

where α is the calibration coefficient which is dependent upon coil and sample geometry. The root mean squared voltage is V_{rms} which is from the sensing coils. In the denominator, the sample mass, m , is multiplied by the magnetic field set by the operating parameters, H_{rms} , for an AC field the frequency, f , also appears in the denominator (12).

2.4. Resistivity Measurements

DC resistivity measurements are also performed on the Lakeshore 7225 utilizing a different sample probe. The resistivity probe contains its own temperature sensor (silicon diode type) and electrical connections for negative and positive current and voltage leads. Samples are either tied or cemented with a small amount of Duco cement to the 4-pin sample card provided by Lakeshore. The 4-pin card plugs into the sample probe interior through a 2 inch notch in the cylinders wall.

The 4 probe method is performed on rectangular samples. The standard geometry is used, a current lead is attached on the long face of the rectangular specimen near each end, one positive, I^+ , and one negative, I^- , lead. Two more electrical leads, V^+ and V^- , are attached inside the ends of the imaginary line segment between I^+ and I^- . Silver paint was used to mate the 2 mil Pt lead wire to the sample surface. Once mounted and plugged into the probe the sample and probe are wrapped in Teflon tape to avoid losing the sample/card should either become loose during operation. After inserting the probe into the cryostat the probe is connected to the computer via the appropriate connectors. Again, all drivers are controlled by the system software.

3. DATA ANALYSIS AND INTERPRETATION

Magnetic and nonmagnetic heat capacities, DC susceptibilities, magnetization, and resistivity measurements on RPdBi, where R = La, Nd, Gd, Dy, Er, and Lu, have been taken for temperatures ranging from ~2K to room temperature, the results of which are discussed in this chapter.

3.1. Heat Capacity

Nonmagnetic heat capacity measurements from ~2 or 4K to room temperature have been conducted on RPdBi where R = La, Nd, Gd, Dy, Er, and Lu. Also, the magnetic field dependence of the heat capacities for GdPdBi and DyPdBi have been measured at fields up to 9.8T.

The heat capacity at constant pressure, C_p , is the experimentally measured value. However, at temperatures ~2-4K $C_p = C_v$, the heat capacity at constant volume which is more frequently used for thermodynamic calculations. The total heat capacity, C_T , for a metallic matrix is comprised of several components (13).

$$C_T = C_p = C_l + C_e + C_m \quad (6)$$

C_l is the lattice contribution to the total. Below temperatures of $\Theta_D/50$, where Θ_D is the Debye temperature, the lattice contribution is found to be

$$C_1 = \beta T^3 \quad (7)$$

where,

$$\beta = \frac{12\pi^4 nR}{5\Theta_D^3} \quad (8)$$

R is the gas constant and n is the number of atoms per molecule.

C_e is the contribution from the conduction electrons and is expressed as

$$C_e = \gamma T \quad (9)$$

where γ is the electronic specific heat coefficient.

Finally, C_m is the magnetic contribution. The form of C_m is dependent upon the type of magnetic ordering encountered. For antiferromagnetic materials the magnetic contribution is expressed as

$$C_m = \delta T^3 \quad (10)$$

However, the rigor of the T^3 law may be spoiled by exchange-coupling anisotropy (14). The total heat capacity may now be written as

$$C_T = \gamma T + \beta T^3 + \delta T^3 \quad (11)$$

This is usually graphed C_T/T vs. T^2 . Fitting a straight line to low temperature data the Debye temperature and electronic specific heat coefficient can be calculated.

For the lanthanides, and their alloys and compounds, it is assumed that the lattice and electronic contributions vary linearly across the series. Separation of the magnetic component from the total heat capacity may then be accom-

plished by subtracting the prorated lattice and electronic contributions from the total (15,16). The lattice and electronic components of the magnetic members of the series are estimated by a weighted sum of the total heat capacities of LaPdBi and LuPdBi:

$$C_{l+e} = XC_p^{LaPdBi} + (1-X)C_p^{LuPdBi} \quad (12)$$

where X is found by equating the molecular weight of the magnetic member to complimentary proportions of LaPdBi and LuPdBi's molecular weight:

$$X = \left(\frac{M_{RPdBi} - M_{LuPdBi}}{M_{LaPdBi} - M_{LuPdBi}} \right) \quad (13)$$

Figure 1 shows the total heat capacity for LaPdBi and LuPdBi from which the lattice and electronic contributions of the magnetic lanthanides are calculated. Plotting C/T v.s. T^2 for the low temperature data ($\leq 5K$), Debye temperatures and electronic specific heat coefficients for LaPdBi and LuPdBi were calculated by a least squares fitting for temperatures ranging from 1.9K to 5K. For LaPdBi $\Theta_D = 228.4 \pm (21.2)K$ and $\gamma = 2.67 \pm (0.50)mJ/mol-K$. LuPdBi has $\Theta_D = 211.1 \pm (25.6)K$ and $\gamma = 1.97 \pm (0.95)mJ/mol-K$. Extending the range for the least square fitting to 10K the values become: $206.4 \pm (3.3)K$ and $1.16 \pm (.25)mJ/mol-K$ for LaPdBi; $194.9 \pm (2.5)K$ and $0.096 \pm (0.327)mJ/mol-K$ for LuPdBi. Figure 2 demonstrates a least squares fitting for the extended temperature range. LaPdBi shows an obvious nonlinearity unfortunately, while LuPdBi remains linear down to $\sim 3K$. In spite of the curvature in the

Figure 1. Heat capacities of LaPdBi and LuPdBi. Inset: shows linear behavior of C/T vs. T^2 for both compounds.

Figure 2. C/T vs. T^2 for temperatures up to 10K. Reference lines shown to highlight any departure from linearity.

the LaPdBi data, the standard deviations are comparable to those of the LuPdBi compound. Extending the data to temperatures above $\Theta_D/50$ ($\sim 4.5K$) decreases the errors in the Θ_D values. However, a linear fitting does not work well for LaPdBi, and LuPdBi deviates at its lowest temperature region. The up-turn suggests that these may be spin fluctuations due to Pd and possibly La and Lu. All of these metallic elements exhibit spin fluctuations in their elemental states, specifically Pd and La, as demonstrated by deviations in γ from the "free electron" value γ_0 . Enhancement factors for Pd, and La and Lu, may be found in references (17) and (18) respectively.

Subtraction of the calculated lattice and electronic contributions from the total heat capacity data is illustrated in Figure 3, for DyPdBi. The slow drop off in the magnetic contribution, C_m , above the magnetic transition ($\sim 4K$) may be due to crystalline field effects or spin fluctuations. The magnetic contribution for the remaining magnetic members are shown in Figure 4, including C_m for DyPdBi. Contributions from the crystalline field plus spin fluctuations are pronounced for NdPdBi and ErPdBi. There is no crystal field contributions from Gd in GdPdBi because $L=0$ for the $4f^7$ configuration. Hence, there is no excess heat capacity above the magnetic ordering temperature. The total magnetic entropy, S_{mag} , has been calculated via

$$S(T) = \int_0^T \left(\frac{C_{mag}}{T} \right) dT \quad (14)$$

Figure 3. Subtraction of C_{l+e} from C_T for DyPdBi to estimate the magnetic component of the heat capacity, C_m .

Figure 4. C_m for all magnetic RPdBi samples. The legend within the inset applies to both graphs. Inset: displays the heat capacity behavior below 20K.

and may be compared to their theoretical values from equation (2). The data for each heat capacity curve was extrapolated linearly from the lowest temperature data point to 0K for the entropy calculation. The entropies associated with magnetic ordering, S_{MO} , and crystalline field(or possibly spin fluctuations), S_{CF} , have also been estimated. These values are listed in Table 4. Also included is the magnetic ordering temperatures, T_{MO} , defined as the temperature where the maximum heat capacity, C_{max} , in the ordering region occurs. Magnetic entropy as a function of temperature is shown in Figure 5 for the magnetic compounds.

The entropies for the Gd and Dy samples are remarkably close to their theoretical values (the Gd value is calculated from 0 to 100K). The significant decrease in the percentage for ErPdBi arise from its low ordering temperature.

Table 4. Ordering Temperatures and Entropies

RPdBi	T_{MO} (K)	C_{max} (J/mol-K)	S_{Theory} (J)	S_{mag} (J)	S_{MO} (J)	S_{CF} (J)	%Theor y
Nd	3.2	8.4	19.15	16.09	6.41	9.68	82.5
Gd	12.5	23.1	17.29	17.25	17.25	0	99.7
Dy	3.7	48.9	23.05	22.64	14.92	7.72	98.2
Er	<1.3	-	23.05	>18.60	>5.76	12.84	>80.7

ErPdBi orders at ~1.3K which is just below the temperature range of the calorimeter used to take the data. The linear extrapolation to 0K for the heat capacity curve of ErPdBi does not fully represent the true behavior. Similarly,

Figure 5. Magnetic entropy as a function of temperature.

for NdPdBi the lowest temperature portion of the transition peak is just beyond the experimental limitations of the calorimeter used. Conversely, the extrapolation for DyPdBi and GdPdBi may introduce a minimal overestimation of the heat capacity for the low temperature ($<1.8\text{K}$) region.

Additional lower temperature data would likely show that the entropies for Er and Nd approach their theoretical values more closely. Also, Nd measurements consist of ~ 2 data points/degree K below 20K while for the remaining compounds $\sim 3-4$ data points/degree K were measured. This may have resulted in a decrease in the measured entropy for NdPdBi due a less refined description of the ordering peak. Finally, the entropy for ErPdBi was calculated to a temperature of 160K, where C_m reaches a value of zero. Figures 3, 4, and 5 only show the data to 100K.

M. Bouvier et al. have shown that the entropy associated with spin fluctuations, ΔS_{fluct} , for gadolinium compounds is approximately 15% of the theoretical entropy (8). This is determined by comparing the relative proportion of the magnetic entropy above T_N with respect to the total entropy. Using $T_N = 12.5\text{K}$ for GdPdBi, $\Delta S_{\text{fluct}}/R\ln(8) = 11\%$. However, Bouvier defines T_N as the temperature where S_{mag} begins to levels off with a near zero slope. This would be $\sim 16\text{K}$ for GdPdBi according to Figure 5, hence, $\Delta S_{\text{fluct}}/R\ln(8) = 5.1\%$.

Another feature to note on Figure 4 is the GdPdBi curve which dips below zero then slowly climbs out to positive values near zero. There are two reasons this may occur. First, the lattice and electronic contributions to the heat capacity do not vary linearly over the lanthanide series. Second, the errors in the heat capacity data (~ 0.5 to 0.7% at 30K) plus any systematic errors in the polynomial fitting used for prorating the lattice and electronic components may cause the negative deviation.

3.1.1. *Magnetic Field Dependence of C for GdPdBi*

Heat capacity measurements have been taken for temperatures ranging from 2K to 25K under magnetic fields of 0, 2.46, 5.32, 7.53, and 9.85T. Figure 6 shows a C/T vs. T curve for GdPdBi.

There is little field dependence exhibited in the heat capacity. Although, a small shift toward lower temperatures occurs as the magnetic field increases, accompanied by small change in the magnitude of C_T . This is indicative of antiferromagnetic ordering. For GdPdBi, the antiferromagnetic structure is not quenched easily, even by the 9.85T field.

The ordering region also displays two maxima. Similar behavior is reported for isostructural GdPtBi in reference (5). A λ type curve can graphically be imposed on the upper

Figure 6. Heat capacity of GdPdBi as a function of magnetic field and temperature.

sharp peak, from which a curve for the lower, broader, peak can be interpolated. The entropies for the two were graphically estimated to be 7.8 J/mol-K for the upper λ -like peak and 8.4 J/mol-K for the low temperature peak. From this first order approximation it appears the entropies are roughly equal. The broad peak may arise from a second magnetic transition, such as a spin reorientation or a spin flip or flop to another antiferromagnetic or ferromagnetic structure.

3.1.2. Magnetic Field Dependence of C for DyPdBi

Under the same conditions, using the same calorimeter, the magnetic field dependence of the heat capacity for DyPdBi was measured and is shown in Figure 7. Unlike GdPdBi, the low temperature heat capacity is strongly field dependent.

Upon increasing the magnetic field to 2.46T the height of the transition peak drops to approximately one third its zero field value, and the temperature of the heat capacity maximum shifts toward lower temperatures. This would indicate that the magnetic phase transition is antiferromagnetic in origin. However, when the field increases to 5.32T the heat capacity maximum drops by a factor of approximately one half, but the temperature where the maximum occurs increases. This indicates a metamagnetic transition to a ferromagnetic state. Higher fields completely quench the heat capacity anomaly.

Figure 7. Heat capacity of DyPdBi as a function of magnetic field and temperature.

The easily quenched magnetic anomaly presents the possibility of a large magnetocaloric effect, i.e. the adiabatic temperature rise for changes in the applied field which is calculated from the total entropy versus temperature curves at various magnetic fields. The entropy for each curve is calculated by

$$S(T,B) = \int_0^T \left(\frac{C}{T} \right) dT \quad (15)$$

where B is the applied magnetic field. Figure 8 shows the magnetic field dependence of total entropy versus temperature. The magnetocaloric effect is produced on changing the magnitude of the applied magnetic field. The adiabatic temperature change for DyPdBi is shown in Figure 9.

The maximum adiabatic temperature change, $\Delta T_{\max}$, of 7.4K for the 0.00-9.85T field change occurs at 6.7K. For the 0.00-7.53 field change $\Delta T_{\max} = 4.7\text{K}$ at 6.5K, $\Delta T_{\max} = 2.5\text{K}$ at 6.9K for field of 0.00-5.32T, and $\Delta T_{\max} = 0.6\text{K}$ for 0.00-2.26T at 7.4K. The adiabatic temperature change is negative at the low end of the temperature scale. A negative magnetocaloric effect is generally expected for antiferromagnetic materials. Though significant, the adiabatic temperature rise for DyPdBi does not compare well to other active magnetic refrigeration (AMR) materials. GdPd exhibits a $\Delta T_{\max}$ of 10K, for a 10T field change at 40K (19). Also, $\Delta T_{\max}$ for DyPdBi is only 1/2 as large as that for Er_3AlC in the same temperature region (20).

Figure 8. Magnetic field dependence of the total entropy for DyPdBi.

Figure 9. Adiabatic temperature change in DyPdBi for several positive magnetic field changes.

3.2. Magnetic Measurements

Results of DC susceptibility measurements for NdPdBi, GdPdBi, DyPdBi, and ErPdBi are presented in Figures 10, 11, 12, and 13 respectively. Their inverse susceptibilities are shown in Figures 14, 15, 16 and 17 respectively.

The susceptibility and inverse susceptibility curves of NdPdBi show few features. Figure 14 shows NdPdBi to behave as a Curie-Weiss paramagnet from 300K to ~4.5K. A paramagnetic Curie temperature, θ_p , for NdPdBi of -7.7(5)K is suggestive of antiferromagnetic ordering. The effective moment, p_{eff} , calculated from a least squares fit of the inverse susceptibility data was found to be 3.54(8) μ_B , where μ_B is one Bohr magneton. This value agrees well with that found for pure Nd where $p_{eff} = 3.62 \mu_B$. Hysteresis loops were measured over magnetic fields of -4T to 4T for several temperatures, results are shown in Figures 18. The magnetization isotherms show no appreciable hysteresis and do not approach saturation. The low temperature isotherms, Figure 19, indicate NdPdBi is initially antiferromagnetic with a metamagnetic transition to the ferromagnetic state at 0.68T for the 2.3K isotherm.

For GdPdBi, $\theta_p = -47.6(5)$ K and $p_{eff} = 7.98(7) \mu_B$ where the effective moment for pure Gd is 7.94 μ_B . The sample obeys Curie-Weiss law from room temperature to ~13K at which temperature the compound orders antiferromagnetically. This

Figure 10. DC Susceptibility of NdPdBi at temperatures from 4.5K to room temperature.

Figure 11. DC Susceptibility of GdPdBi at temperatures from 4.5K to room temperature. Inset: behavior of χ_{DC} in region of magnetic ordering.

Figure 12. DC Susceptibility of DyPdBi at temperatures from 4.5K to room temperature. Inset: behavior of χ_{DC} in region of magnetic ordering.

Figure 13. DC Susceptibility of ErPdBi at temperatures from 4.5K to room temperature.

Figure 14. Inverse susceptibility for NdPdBi at 0.5T over temperatures from 4.5K to 300K. The regression line represents the Curie-Weiss behavior.

Figure 15. Inverse DC susceptibility of GdPdBi at 0.5T. Inset shows the low temperature behavior of χ_{DC} . Both graphs show a regression line representing Curie-Wiess behavior.

Figure 16. Inverse DC susceptibility of DyPdBi at 0.5T. Inset shows the low temperature behavior of χ_{DC} . Both graphs show a regression line representing Curie-Wiess behavior.

Figure 17. Inverse DC Susceptibility of ErPdBi at temperatures from 4.5K to room temperature.

Figure 18. MH hysteresis loop isotherms for NdPdBi shown in the first quadrant up to a maximum field of 4T.

Figure 19. Low field and low temperature magnetization isotherms for NdPdBi. Inset: shows the slope (dM/dH) versus field.

is seen as a decrease in χ_{DC} below 13K, or increase in $1/\chi_{DC}$ in Figure 15. The antiferromagnetic nature of GdPdBi is also seen in the magnetization loops shown in Figure 20 (i.e. negative curvature in the 4.5K and 8.5K isotherms). Again, there is no appreciable hysteresis for this compound and saturation does not occur.

Calculations for DyPdBi show $\theta_p = -14.0(5)K$ and $p_{eff} = 10.39(6) \mu_B$, which closely agrees with the $10.65 \mu_B$ effective moment of Dy. DyPdBi behaves paramagnetically from room temperature down to $\sim 4K$ where antiferromagnetic ordering occurs. Figure 21, shows the MH isotherms for two temperatures below the T_N and one just above T_N . There is a magnetic field induced ferromagnetic transition at 2.6T, as shown by the inflection point in the first two isotherms. This is consistent with the heat capacity data shown in Figure 5, where there is a change in the nature of the temperature dependence from that measured at 2.46T or lower with C measured at 5.32T or higher. Little hysteresis is shown for DyPdBi, as such, energy losses upon magnetization would be minimal for a magnetocaloric cycle.

Regression output for ErPdBi indicates $\theta_p = -5.0(3)K$ and $p_{eff} = 9.34(8) \mu_B$. The effective moment of ErPdBi agrees well with that for trivalent Er metal at $9.58\mu_B$. The sample obeys the Curie-Weiss Law from $\sim 4.5K$ to room temperature. The negative paramagnetic Curie temperature suggests ErPdBi ground

Figure 20. MH hysteresis loop isotherms for GdPdBi shown in the first quadrant up to a maximum field of 5T. Inset: shows behavior at small fields. Legend and vertical scale units are the same for both graphs.

Figure 21. MH hysteresis loop isotherms for DyPdBi shown in the first quadrant up to a maximum field of 5T. Inset: shows slope (dM/dH) as a function of field.

state is antiferromagnetic. Figure 22, show the MH hysteresis behavior for ErPdBi. Low temperature magnetization data were not taken on this sample since the ordering temperature is below the capabilities of the apparatus, hence the extra data would most likely be un insightful.

Figure 23 plots $|\theta_p|$ and T_N versus the de Gennes factor. Both $|\theta_p|$ and T_N for the limited heavy RPdBi series falls slightly below de Gennes scale but does follow the expected trend. No conclusion about the scaling properties of the light RPdBi series can be made based upon the values of $|\theta_p|$ and T_N for NdPdBi.

AC susceptibility measurements were conducted for GdPdBi and DyPdBi near T_N . For GdPdBi, χ'_{ac} behaved consistently with DC susceptibility and heat capacity data. Figure 24 shows χ'_{ac} for static DC fields between 0 and 5T and an AC field of 1.25 Oe. The susceptibility, χ'_{ac} , showed minimal frequency dependence over a 25 to 1000 Hz range for an AC field of 1.25 Oe, which is seen in Figure 25. The AC susceptibility of DyPdBi also behaved consistently with the DC and heat capacity data. Figure 26 shows χ'_{ac} for static DC fields between 0 and 1T and an AC field of 1.25 Oe. DyPdBi exhibits an AC field frequency dependence as shown in Figure 27, where the low frequency fields produce smaller susceptibilities.

Figure 22. MH hysteresis loop isotherms for ErPdBi shown in the first quadrant up to a maximum field of 5T.

Figure 23. $|\theta_p|$ and T_N for RPdBi as a function of the de Gennes factor for the lanthanide elements.

Figure 24. AC susceptibility for GdPdBi as a function of temperature for several DC magnetic fields.

Figure 25. AC susceptibility for GdPdBi as a function of temperature for several AC field frequencies.

Figure 26. AC susceptibility for DyPdBi as a function of temperature for several DC magnetic fields.

Figure 27. AC susceptibility for DyPdBi as a function of temperature for several AC field frequencies.

3.3. Resistivity Measurements

The DC electrical resistivity for each member of the RPdBi series was measured at or below 4.5K to room temperature using the 4-probe method. Figure 28 shows the resistivity for the lanthanide series normalized by their respective resistivities at 300K. Units for the measured values were on the order of $\text{m}\Omega\text{-cm}$ to $10 \text{ m}\Omega\text{-cm}$ at room temperature, which is two to three orders of magnitude larger than that of typical metallic conductors.

Each of the magnetic rare earth based samples shows a pronounced semiconductor-like increase in resistivity as the temperature decreases until a maximum is reached. Below the maximum the temperature dependence of the resistivity exhibits a metallic-like behavior as the temperature continues to decrease. DyPdBi exhibits the largest resistivity increase at 80K where it is ~ 3.3 times the room temperature value, $\rho(300)$. The next largest rise occurs with ErPdBi, $\sim 2.2\rho(300)$ at 55K, followed by GdPdBi with $\sim 2\rho(300)$ at 65K, then NdPdBi with $\sim 1.4\rho(300)$ at 77K. LuPdBi only rose ~ 1.1 times $\rho(300)$ at 166K. Figure 29 shows the trend graphically.

The behavior of LaPdBi appears anomalous when compared to its nonmagnetic brother LuPdBi. For LaPdBi there is a significant increase in resistivity with two local maxima. The sample used contained $\sim 5\%$ second phase. A pure sample was

Figure 28. Resistivities as a function of temperature for $RPdBi$ compounds. Resistivities have been normalized by values at 300K.

Figure 29. Maximum increase in resistivity as a function of lanthanide atomic number.

not used because the homogenous LaPdBi was used to measure heat capacity, the sample had been powdered and mixed with silver to make the measurement. Attempts at synthesizing a new LaPdBi sample have been unsuccessful, new material is being prepared concurrently with the drafting of this manuscript.

Similar behavior is seen for the RPtBi series discussed in reference 5. However, the trend has the maximum increase occurring for NdPdBi followed by Gd, Tb, Dy, and Yb being metal-like with its resistivity decreasing as the temperature decreases. The transport properties of NdPtBi have been studied by Don Morelli, of General Motors, et al. (21). Morelli describes NdPtBi as a ternary intermetallic semiconductor with a small band overlap at or near the Fermi level. The small overlap gives rise to the semi-metallic behavior with high hole and electron mobilities. The close relationship between the RPdBi and RPtBi series suggests this process may give rise to the behavior seen with the RPdBi series.

An estimate of the energy band gap, E_g , for a semiconductor can be made by modeling the conductivity (or resistivity) in the intrinsic region by

$$\sigma = f(T)e^{-E_g/2k_B T} \quad (16a)$$

or

$$\rho = g(T)e^{E_g/2k_B T} \quad (16b)$$

Taking the natural logarithm equation (16b) becomes

$$\ln(\rho) = \ln[g(T)] + (E_g/2k_B) (1/T) \quad (17)$$

The temperature dependence of $g(T)$ is generally neglected. Plotting the log of the resistivity versus reciprocal temperature provides a measure of the width of the band gap (22). Figures 30 and 31 show the $\ln$ or the reduced resistivity as a function of temperature for the RPdBi series. The energy gaps are calculated from the near room temperature regions show in Figure 32, where $\rho(T)/\rho(300)$ is linear. Values for E_g are listed in Table 5. These values are

Table 5. Energy Band Gaps for RPdBi series

RPdBi	LaPdBi	NdPdBi	GdPdBi	DyPdBi	ErPdBi	LuPdBi
E_g (meV)	135(3)	24.9(4)	32.5(6)	123(2)	34.1(5)	15.2(7)

on the order of $k_B T$ at 300K (~ 26 meV). The band gaps for LaPdBi and DyPdBi are sizable, i.e. $5.2k_B T$ (135meV) and $4.7k_B T$ (122meV) at room temperature relative to the other RPdBi materials but small compared to the Si (1140 meV) and Ge (670 meV). Values for E_g on the order of $k_B T$ may indicate that the measured value is not a band gap energy but ionization potentials for multiple acceptor/donor levels.

It should be noted that the near zero electronic specific heat coefficients for LuPdBi is consistent with the

Figure 30. Natural log of the resistivity as a function of the reciprocal temperature.

Figure 31. Natural log of the resistivity as a function of the reciprocal temperature for temperatures above 100K.

Figure 32. Linear regression lines calculated for the natural log of the resistivity as a function of the reciprocal temperature near room temperature.

semiconductor like behavior exhibited. However, the comparatively larger γ value for LaPdBi implies a more metallic nature for this material. This inconsistency may be due to the minor second phase contained within the LaPdBi sample used for the resistivity measurements.

The semiconductor-like behavior of the ternary (1,1,1) intermetallic has prompted investigations of the electronic behavior of these materials. Morelli's interest in NdPtBi is the potential moderate-temperature thermoelectric applications of this material. Bruce Cook and Joel Harringa, of Ames Laboratory's Conversion Technology program, measured the room temperature Seebeck coefficients, S , of LaPdBi, NdPdBi, GdPdBi, DyPdBi, ErPdBi, and LuPdBi, and were found to be 166.4, 90.2, 138.8, 89.8, 85.3, and 63.6 $\mu\text{V}/\text{C}$ respectively. The positive values indicate that these materials are p-type semiconductors. The thermoelectric power factor ($S^2\sigma$ or S^2/ρ) has been calculated using the room temperature resistivity values: the thermoelectric power factors are 27.7, 4.5, 37.0, 4.0, 10.4, and 3.7 $\mu\text{W}/\text{cmC}^2$ respectively. These values are tabulated graphically on Figure 33.

Conventional thermoelectric energy conversion has been provided by silicon-germanium alloys in radioisotope thermoelectric generators (RTGs), generally for space exploration applications (23). Generators composed of $\text{Si}_{80}\text{Ge}_{20}$ doped with GaP and P have Seebeck coefficients ranging from approximately

Figure 33. Seebeck coefficient and Thermopower factor as a function of lanthanide atomic number.

-195.0 to over -240 $\mu\text{V}/\text{C}$; with thermoelectric power factors on the order of 30 $\mu\text{W}/\text{cmC}^2$ (24). LaPdBi and GdPdBi have values comparable to the silicon-germanium alloys and which may be of interest to, and warrant further study by the Ames Laboratory's Conversion Technology program.

3.3.1. *Magnetoresistance*

Resistivity as a function of temperature and magnetic field has been measured for NdPdBi, GdPdBi, DyPdBi, and ErPdBi and shown in Figures 34, 35, 36, and 37 respectively. It should be noted that Figures 35-37 show the absolute resistivity at zero magnetic field for each sample, i.e. not normalized by the room temperature value as shown in Figures 28-32. The variation in absolute magnitude may in part arise from nonuniform junction resistance associated with the silver paint contacts. Furthermore, the absolute resistivity for NdPdBi was estimated due to the misshapen nature of the sample. Absolute resistivity values for LuPdBi and LaPdBi are tabulated in the appendix.

NdPdBi exhibits a slight increase in resistivity as the magnetic field increases. However at lower temperatures, $<40\text{K}$ there is a minor decrease in the resistance with increasing magnetic field. The magnetoresistance is represented better by graphing $\Delta\rho/\rho \equiv [\rho(H) - \rho(0)]/\rho(0)$ versus temperature, where

Figure 34. DC resistivity as a function of temperature and magnetic field for NdPdBi.

Figure 35. DC resistivity as a function of temperature and magnetic field for GdPdBi. Inset: shows resistivity about T_N .

Figure 36. DC resistivity as a function of temperature and magnetic field for DyPdBi. Inset: shows resistivity about T_N .

Figure 37. DC resistivity as a function of temperature and magnetic field for ErPdBi.

$\rho(0)$ is the zero field resistivity and $\rho(H)$ is the resistivity under an applied field H (25). Figure 38 shows $\Delta\rho/\rho$ for NdPdBi. As above, two distinct features are seen. First, at temperatures below 40K and approaching the ordering temperature the resistivity decreases. This effect arises due to the decreased scattering of the conduction electrons from the randomly aligned magnetic moments. As the fields increase (at low temperatures) the paramagnetic randomization and spin fluctuations decrease. Above 40K the magnetic field increases the resistivity which may arise from the lifting of crystal-line field degeneracies or enhancing CEF anisotropy. The temperature where $\Delta\rho/\rho$ changes sign may be indicative of the competition between the two processes.

GdPdBi shows significant magnetoresistance. The resistivity maximum decreases as the magnetic field increases. There is also a slight upward shift in the temperature of $\rho_{\max}$ as the magnetic field increases. The change in slope of the resistivity curve near 14K arises from the magnetic ordering. The trend for $\Delta\rho/\rho$ is shown on Figure 39. The resistivity steadily decreases with increasing field, almost 20% for a 4T field at 4.5K. Noticeably absent is the rise in resistivity at higher temperatures. The slight resistivity increase shown above 150K is only 0.5% for the 4T field is well within experimental error limits. This absence is due to the lack of

Figure 38. Magnetoresistance, $\Delta\rho/\rho$, as a function of field and temperature for NdPdBi.

Figure 39. Magnetoresistance, $\Delta\rho/\rho$, as a function of field and temperature for GdPdBi. Inset:

CEF effects and anisotropies in Gd compounds and serves to bolster the the proposed explanation for the behavior of $\Delta\rho/\rho$ for NdPdBi.

DyPdBi shows a similar shift in the temperature of $\rho_{\max}$, however the magnitude of $\rho_{\max}$ increases slightly. The resistivity slowly rises below T_N . There are no data for ρ at 4T below 4.3K due to problems operating the magnet at sub liquid-helium temperatures. The magnetoresistance is highlighted in Figure 40, and appears similar to that of NdPdBi. However, the magnitude of the resistivity decrease at low temperatures ($\leq 50K$) is larger and the rise in resistivity associated with CEF is shorter lived, amounting to 1-2% between $\sim 80K$ and 225K.

ErPdBi behaved much the same way as the Nd and Dy samples. The magnetoresistance, shown in Figure 41, exhibits increased resistivity starting at $\sim 50K$ and persisting to room temperature. However, the magnitude of the $\Delta\rho/\rho$ is larger for ErPdBi than NdPdBi.

Figure 40. Magnetoresistance, $\Delta\rho/\rho$, as a function of field and temperature for DyPdBi. Inset: shows behavior of near ordering temperature.

Figure 41. Magnetoresistance, $\Delta\rho/\rho$, as a function of field and temperature for ErPdBi.

4. CONCLUSIONS

The results on this study on RPdBi ternary intermetallic compounds, where $R = \text{La, Nd, Gd, Dy, Er, and Lu}$, show that each magnetic species to have an antiferromagnetic ground state with a low ordering temperature. This has been demonstrated by the behaviors of heat capacities and magnetic susceptibilities. Both DyPdBi and NdPdBi display a metamagnetic phase transition to a ferromagnetic state at 2.6T and 0.68T, respectively. The magnetic moments are in close agreement with those of the constituent magnetic ions. Also, the entropy utilized during magnetic ordering (and CEF/spin fluctuation) is highly efficient for GdPdBi and DyPdBi. All of these materials are magnetically soft. T_N and $|\theta_p|$ do not closely follow the de Gennes factor, but follow the general trend. DyPdBi has properties that produce a sizable magnetocaloric effect which is insufficient for use as a low temperature active magnetic regenerator (AMR) when compared to current AMR materials.

Resistivity measurements indicate semiconductor like behavior above $\sim 150\text{K}$ and metallic like resistivities below $\sim 50\text{K}$. Band gaps calculated at room temperature are on the order of $0.5k_B T$ to $5k_B T$. If these materials are truly in a new class of ternary intermetallic semiconductors the effect of impurities will need to be considered for a more careful

study of their electrical properties (i.e. study of RPdBi series synthesized from ultrapure constituents).

The large thermal electric power factors for GdPdBi and LaPdBi may suggest possible applications as thermoelectric generators (materials cost not being a factor). Further study of their thermoelectric properties may prove interesting.

The magnetoresistance for the magnetic members demonstrates the competition between CEF and spin fluctuations /magnetic ordering on increasing or reducing electron scattering.

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APPENDIX

Absolute dc resistivity values for LuPdBi and LaPdBi.

LuPdBi		LaPdBi	
Temperature (K)	DC Resistivity (m Ω -cm)	Temperature (K)	DC Resistivity (m Ω -cm)
4.69	1.136	4.68	3.150
5.71	1.136	5.71	3.149
6.74	1.136	6.74	3.149
7.77	1.136	7.77	3.150
8.82	1.137	8.83	3.149
9.85	1.137	9.87	3.154
10.77	1.138	10.91	3.157
11.26	1.138	11.95	3.161
12.07	1.139	12.99	3.166
13.08	1.140	14.04	3.172
14.04	1.140	14.89	3.178
16.98	1.143	14.91	3.190
19.88	1.146	15.59	3.200
22.81	1.149	18.48	3.225
25.72	1.151	21.40	3.248
28.63	1.154	24.29	3.275
33.59	1.158	27.53	3.293
38.41	1.161	30.61	3.315
43.25	1.165	35.69	3.325
47.89	1.168	40.75	3.328
53.40	1.172	45.46	3.323
58.60	1.175	49.78	3.314
63.48	1.178	53.71	3.303
68.27	1.180	57.46	3.282
73.10	1.183	63.27	3.260
78.04	1.185	68.27	3.237
83.06	1.187	73.06	3.214
87.80	1.189	77.99	3.188
92.51	1.191	83.10	3.165
97.39	1.193	87.88	3.142
106.99	1.198	92.58	3.128
117.56	1.202	97.50	3.120
127.60	1.206	107.40	3.078
137.22	1.209	118.09	3.039
146.92	1.212	127.97	3.009
156.55	1.213	137.73	2.984
166.19	1.214	147.39	2.962
175.95	1.214	156.95	2.940
185.68	1.213	166.63	2.912

Temperature (K)	DC Resistivity (Ω -cm)	Temperature (K)	DC Resistivity (Ω -cm)
195.59	1.210	176.38	2.871
205.56	1.206	186.09	2.809
215.67	1.199	195.97	2.720
225.70	1.192	205.93	2.597
235.70	1.183	216.00	2.442
245.75	1.172	226.00	2.265
255.79	1.161	235.98	2.076
265.97	1.148	246.09	1.885
276.09	1.133	256.11	1.705
286.12	1.118	266.17	1.538
296.26	1.103	276.28	1.383
306.42	1.089	286.34	1.245
316.60	1.079	296.40	1.128
-	-	306.58	1.021
-	-	316.87	0.927