# Low temperature heat capacity of $YPb_3$, $LaPb_3$, $La_5Pb_3$ and $La_5Pb_3C$

by

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# INTRODUCTION

In the last six years, eight of the seventeen rare earth-lead binary phase diagrams (1-9) have been investigated at the Ames Laboratory-USAEC, Iowa State University, Ames, Iowa. These investigations revealed a variety of intermetallic compounds in the different systems with the number and composition of the compounds varying from system to system. In addition several investigators (10-25) have determined the lattice parameters for many of the rare earth-lead compounds. This work has been summarized by Gschneidner and McMasters (26) who indicated trends in the data that point to occurrence or absence of certain compounds in the systems. Very little work has been done on these alloys other than the phase diagram determinations and crystal structure studies. The heat capacity measurements on the $LaSn_3$ and $LaPb_3$ compounds ($AuCu_3$ structure type) were performed by Bucher et al. (27) as part of an investigation of magnetic impurities in superconductors. Gambino et al. (17) determined the lattice parameters, superconducting transition temperatures and interatomic distances in the same compounds. The superconducting transition in $YPb_3$ was reported by Havinga (28) and Havinga et al. (29). In addition Havinga et al. (29) give values for the room temperature susceptibilities and thermoelectric power for $YPb_3$ and $LaPb_3$.

The occurrence or nonoccurrence of some phases has been attributed to the influence of the 4f electrons in the lanthanide series (26). To support or refute this proposal much additional data are needed. In an effort to obtain some of these data heat capacity measurements were undertaken. Hopefully, this investigation is the first of a series of

studies which will provide a better understanding of these lanthanide compounds. The compounds chosen for this investigation were $YPb_3$, $LaPb_3$ and $La_5Pb_3$. After the heat capacities of these compounds had been measured the heat capacity of a fourth compound $La_5Pb_3C$ was measured to see if it would be helpful in understanding the $La_5Pb_3$ results.

Low temperature heat capacity measurements were chosen because they provide information about the vibrational and electronic behaviors of all materials and for some materials about their magnetic, crystal field and nuclear properties. At low temperatures (1-20°K) (30) the temperature dependence of the heat capacity of a normal, metallic material is as follows:

$$C_p = C_v = \gamma T + \beta T^3 = C_e + C_l. \qquad (1)$$

$C_e$ or $\gamma T$ is the electronic contribution and $\gamma$, the electronic specific heat constant, is proportional to the density of states at the Fermi energy $n(E_F)$. $C_l$ or $\beta T^3$ is the lattice contribution and $\beta$ is given by

$$\beta = \frac{12\pi^4 R}{5\Theta_D^{o\,3}} \qquad (2)$$

if the heat capacity is given in units per g at. In Equation 2, R is the gas constant and $\Theta_D^o$ is the Debye characteristic temperature. The lattice term is the low temperature limit of the Debye model of a solid as an isotropic elastic continuum where the distribution of vibrational modes in the lattice is proportional to square of the frequency. Plotting data as C/T vs $T^2$ (i.e., dividing Equation 1 through by T) should yield a

straight line at low temperatures where the intercept is $\gamma$ and the slope is $\beta$. Theoretically the Debye model should hold (i.e., Equation 1 is valid) up to temperatures of $\Theta_D^o/10$. But from the many heat capacity experiments that have been done it has been observed that the approximation is applicable in general only to temperatures up to 1/30th to 1/20th of the Debye temperature.

If an element or one of the elements in a compound has an unpaired inner electron, such as a 4f electron for the rare earth metals, and the material orders magnetically, then there is a magnetic contribution to the specific heat. This contribution according to simple spin wave theory has a $T^{3/2}$ temperature dependence for a ferromagnet or a $T^3$ dependence for an antiferromagnet. Furthermore, for compounds which contain a lanthanide element which has an unpaired 4f electron, additional contributions to the heat capacity may occur because of thermal excitation to higher electron (Schottky anomaly) or nuclear (nuclear hyperfine specific heat) energy levels.

At this initial stage of investigation the properties of rare earth-lead compounds, the electronic and vibrational characteristics, are of prime importance. Thus, because of the possibility of additional contributions to the heat capacity from compounds containing rare earths which have one or more unpaired 4f electrons, our study was limited to rare earth-lead compounds which contained scandium, yttrium, lanthanum or lutetium. The lanthanum compounds were selected because their lattice and electronic contributions to the heat capacities would be expected to be representative for the corresponding rare earth-lead compounds, and

later heat capacity investigations could deal with the magnetic contributions that arise with the filling of the 4f shell. Yttrium is similar to the heavy lanthanides in size but not in mass and this is important when considering the Debye temperature. It would have been better to have measured $LuPb_3$ as a typical representative of the heavy rare earth metals but unfortunately this compound does not exist. $YPb_3$ does, however, provide some interesting discussion when it is compared to $LaPb_3$.

The 5:3 and 1:3 (rare earth to lead ratio) compounds were chosen because they represented the most frequently occurring compounds in the trivalent rare earth-lead systems, they were the compounds of lowest and highest lead composition and in most systems they were the compounds with the highest (5:3) and lowest (1:3) melting points.

The structure and lattice parameters for $YPb_3$ (22,25) and $LaPb_3$ (5,16,17) have been reported previously. These two compounds have the cubic $AuCu_3$ structure with the rare earth atoms located at the corners of the cube (0,0,0) and the lead atoms on the faces (1/2,0,1/2; 1/2,1/2,0; 0,1/2,1/2). Gschneidner and McMasters (26) reported lattice parameters for these compounds of $\underline{a}_o = 4.818 \pm .005$ Å and $\underline{a}_o = 4.904 \pm .002$ Å respectively.

$La_5Pb_3$ has the hexagonal $D8_8$ or $Mn_5Si_3$ type structure with $\underline{c}/\underline{a} < 1$ (5,10), and lattice parameters of $\underline{a}_o = 9.526 \pm .002$ Å and $\underline{c}_o = 6.994 \pm .001$ Å (26). The lanthanum and lead atoms are located in the following positions in the unit cell:

| | | |
|---|---|---|
| La(1): | 4 d | 1/3,2/3,0; 2/3,1/3,0; 1/3,2/3,1/2; 2/3,1/3,1/2. |
| La(2): | 6 g | x,0,1/4; 0,x,1/4; $\bar{x}$,$\bar{x}$,1/4; $\bar{x}$,0,3/4; 0,$\bar{x}$,3/4 x,x,3/4. |
| Pb: | 6 g | as above. |

Hohnke and Parthé (31) in their paper on the $D8_8$ rare earth-bismuth-copper compounds pointed out that the lattice could be constructed of octahedra formed by surrounding each bismuth (lead) atom with six rare earth atoms and stacking these octahedra in the c direction. They also pointed out that the distances between the rare earth atoms in the 4d positions in the c direction were less than the metallic radii derived from the pure elements. They found that the rare earth and bismuth atoms occupied the positions noted above for the lanthanum and lead atoms respectively. When they added copper atoms to the structure these atoms went into the "holes" in the lattice at 0,0,0 and 0,0,1/2 or the 2b sites. The addition of the atoms caused the a lattice parameter to expand, but the c lattice parameter remained constant within a few thousandths of an angstrom. This particular structure was referred to as the "filled" $D8_8$ structure which had been reported earlier by Reiger et al. (32) for the $Hf_5Sn_3Cu$ compound. Nowotny and Benesovsky (33) in a review article refer to this structure as being made up of octahedra of 6 atoms surrounding the atom in the 2b site.

It is proposed that the $La_5Pb_3C$ compound has this "filled" $D8_8$ structure although it has not been reported in the literature. Extrapolated lattice parameters obtained from X-ray powder patterns show that the

carbon atoms do not distort the structure appreciably, but neutron diffraction data would be needed for absolute proof that the carbons are in the 2b positions.

## SAMPLE PREPARATION

All samples used in this investigation were prepared by casting weighed amounts of the pure metals in tantalum crucibles. The rare earths were produced here at the Ames Laboratory by calcium reduction of the rare earth trifluorides. The lead used was purchased from Comnico Products, Co. The carbon used in preparing $La_5Pb_3C$ was spectroscopically pure carbon and its analysis is listed in Table 1 along with those of the rare earths and lead. The rare earths are listed by batch number and the impurities are listed in ppm atomic.

The congruently melting compounds, $La_5Pb_3$ and $LaPb_3$, were heated inductively, inverted, heated again for at least three cycles and then heat treated below the lowest peritectic or eutectic horizontal adjacent to the compound in order to insure homogeneity. The photomicrographs, Figures 1, 2 and 3, show that the resultant alloys are essentially single phase compounds. $YPb_3$ presented more problems because it is a peritectically melting compound. The component metals were heated inductively to the liquid range, cooled and heated again. Each time the sample was held in the liquid range for about 30 min. This cycle was repeated three times and instead of slow cooling on the last cycle the sample was quenched by turning off the power to the induction coil and back filling the vacuum system with argon. After heat treating the sample for more than three weeks at 25°C below the melting point of 740°C, the peritectic structure disappeared leaving an essentially one phase alloy with only a small amount of second phase (see Figure 4).

Since preliminary measurements on $La_5Pb_3$ suggested that the Debye

Table 1. Chemical analysis of components (impurity levels are given in atomic ppm)

| Impurity | Starting Materials | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | La | | | | Y | | C | Pb |
| | JC-1-112 | JC-2-14 | JC-4-79 | LA-6471 | JC-1-101 | JC-3-4 | | |
| H | 2 | 18 | 444 | 6 | 19 | -[a] | - | - |
| Li | - | - | - | < .01 | - | - | - | - |
| Be | 0.4 | ≤ 0.2 | 0.1 | ≤ .05 | - | < 1 | - | - |
| B | 0.3 | ≤ 0.1 | - | 0.3 | - | 0.5 | - | - |
| C | 625 | 486 | 90 | 254 | 650 | ND | M[b] | - |
| N | 8 | 193 | 77 | 41 | 18 | 50 | - | - |
| O | 40 | 219 | 682 | 203 | 1000 | 600 | - | - |
| F | 12 | 5 | 80 | 10 | 6 | 4 | - | - |
| Na | 2 | 10 | 40 | - | 2 | 10 | - | - |
| Mg | 2 | 5 | 0.3 | ≤ 0.1 | 20 | 4 | 0.6 | 0.1 |
| Al | 20 | 6 | 6 | 2 | 50 | 30 | 0.4 | ND |
| Si | 70 | 10 | 17 | 1 | - | 20 | 0.4 | 0.1 |
| P | 1 | < .1 | 0.03 | < 0.1 | - | 0.2 | - | - |
| S | ≤ 10 | < 4 | - | 0.6 | - | 0.5 | - | - |

[a] - not analyzed for.

[b] M major component.

Table 1. (Continued)

| Impurity | Starting Materials | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | La | | | | Y | | C | Pb |
| | JC-1-112 | JC-2-14 | JC-4-79 | LA-6471 | JC-1-101 | JC-3-4 | | |
| Cl | 30 | 4 | 60 | 4 | 20 | 10 | - | - |
| K | 10 | 10 | 1 | 0.2 | 3 | 3 | - | - |
| Ca | 4 | 4 | 3 | 0.2 | 4 | 2 | - | - |
| Sc | 0.5 | < 2 | 0.3 | ≤ 0.1 | 3 | 10 | - | - |
| Ti | 15 | 1 | 4.0 | 1.0 | - | 0.1 | - | - |
| V | 0.2 | 0.2 | - | 0.08 | 30 | 0.5 | - | - |
| Cr | 0.7 | 3 | 10 | 0.3 | 50 | 10 | - | ND |
| Mn | 0.2 | 2 | 0.2 | 0.03 | 2 | 0.1 | - | ND |
| Fe | 40 | 30 | 1.6 | 5 | 318 | < 200 | 0.6 | 0.1 |
| Co | 0.4 | 0.1 | 0.5 | < 0.08 | 80 | 0.2 | - | - |
| Ni | 30 | 3 | 2.0 | 0.9 | 80 | 20 | - | ND |
| Cu | 5 | 3 | 5 | 0.5 | 20 | 20 | - | 0.2 |
| Zn | 0.2 | 0.8 | 0.4 | 0.07 | 8 | 0.2 | - | - |
| Ga | ND | < 1 | - | - | - | ≤ 0.05 | - | - |
| Ge | ND | < .1 | - | < 0.2 | - | ≤ 0.1 | - | - |
| As | ND | < .1 | - | < 0.04 | - | ≤ 0.02 | - | - |
| Se | ND | < 0.1 | - | < 0.06 | - | ND | - | - |
| Br | 0.4 | < 0.6 | - | 0.1 | - | < 0.1 | - | - |

Table 1. (Continued)

| Impurity | Starting Materials | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | La | | | Y | | | C | Pb |
| | JC-1-112 | JC-2-14 | JC-4-79 | LA-6471 | JC-1-101 | JC-3-4 | | |
| Rb | ND | ND | - | < 0.04 | - | ND | - | - |
| Sr | ND | ND | - | < 0.06 | - | ND | - | - |
| Y | 4 | 0.2 | 3 | 2.0 | M | M | - | - |
| Zr | 1 | ≤ 0.1 | ND | < 0.4 | - | ND | - | - |
| Nb | ≤ 5 | ≤ 40 | - | - | - | ≤ 5 | - | - |
| Mo | 7 | - | ND | < 2 | - | ND | - | - |
| Tc | - | - | ND | - | - | ND | - | - |
| Ru | ND | - | ND | < 1 | - | ND | - | - |
| Rh | ND | - | ND | < 0.2 | - | 2 | - | - |
| Pd | ND | - | ND | < 0.4 | - | ND | - | - |
| Ag | ND | 8 | ND | < 0.1 | - | ND | - | 0.1 |
| Cd | ND | - | ND | < 0.1 | - | ND | - | ND |
| In | ND | - | ND | < 0.08 | 4 | ND | - | ND |
| Sn | 0.3 | - | ND | < 0.4 | - | ND | - | ND |
| Sb | ND | - | ND | < 0.08 | - | ND | - | ND |
| Te | ND | - | ND | < 0.1 | - | ND | - | - |
| I | ND | 0.06 | ND | < 0.06 | - | ND | - | - |
| Cs | ND | - | ND | < 0.04 | - | ND | - | - |
| Ba | ND | - | ND | < 2 | 0.3 | ND | - | - |

Table 1. (Continued)

| Impurity | Starting Materials | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | La | | | Y | | C | Pb | |
| | JC-1-112 | JC-2-14 | JC-4-79 | LA-6471 | JC-1-101 | JC-3-4 | | |
| La | M | M | M | M | 40 | 1 | - | - |
| Ce | ≤ 10 | 10 | 30 | 27 | 90 | 0.6 | - | - |
| Pr | ≤ 20 | 30 | 3 | 2.2 | 4 | 0.2 | - | - |
| Nd | ≤ 10 | 10 | 40 | 1 | 8 | 1 | - | - |
| Sm | 4 | < 0.6 | - | < 0.3 | 1 | ND | - | - |
| Eu | 2 | ≤ 2 | 0.8 | ≤ 0.2 | 0 | ND | - | - |
| Gd | 4 | ≤ 1 | 30 | 1.0 | 50 | 4 | - | - |
| Tb | 2 | ≤ 3 | 0.3 | 0.9 | 20 | 1 | - | - |
| Dy | ND | 7 | 4 | < 3 | 2 | 0.8 | - | - |
| Ho | 1 | 2 | 1 | ≤ 0.3 | 3 | 2 | - | - |
| Er | 1 | 1 | 1 | 1 | 30 | 1 | - | - |
| Tm | ND | 3 | - | 0.1 | 1 | ND | - | - |
| Yb | 2 | < 1 | .1 | 0.1 | 2 | ND | - | - |
| Lu | 5 | 3 | - | ≤ 2 | 9 | 1 | - | - |
| Hf | ≤ 2 | - | - | < 0.8 | 9 | ND | - | - |
| Ta | ≤ 70 | 15 | 10 | 9 | 100 | 3 | - | - |
| W | 20 | - | - | ≤ 40 | - | 10 | - | - |
| Re | ND | - | - | < 1 | - | ND | - | - |

Table 1. (Continued)

| Impurity | Starting Materials | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | La | | | | Y | | C | Pb |
| | JC-1-112 | JC-2-14 | JC-4-79 | LA-6471 | JC-1-101 | JC-3-4 | | |
| Os | ND | - | - | < 1 | - | ND | - | - |
| Ir | ND | - | - | < 0.6 | 1 | ND | - | - |
| Pt | ND | - | - | 0.3 | 20 | ND | - | - |
| Au | ND | - | - | 0.1 | 3 | ND | - | - |
| Hg | ND | - | - | 0.2 | 3 | ND | - | - |
| Tl | ND | - | - | < 0.1 | - | ND | - | 0.2 |
| Pb | 2 | - | - | 0.1 | 5 | 0.2 | - | - |
| Bi | ND | - | - | < 0.08 | 1 | ND | - | 0.1 |
| Po | - | - | - | < 0.2 | - | ND | - | - |
| At | - | - | - | < 0.2 | - | ND | - | - |
| Fr | - | - | - | - | - | ND | - | - |
| Ra | - | - | - | - | - | ND | - | - |
| Ac | - | - | - | - | - | ND | - | - |
| Th | 3 | - | - | - | - | ND | - | - |
| Pa | - | - | - | - | - | ND | - | - |
| U | ND | - | - | - | - | ND | - | - |

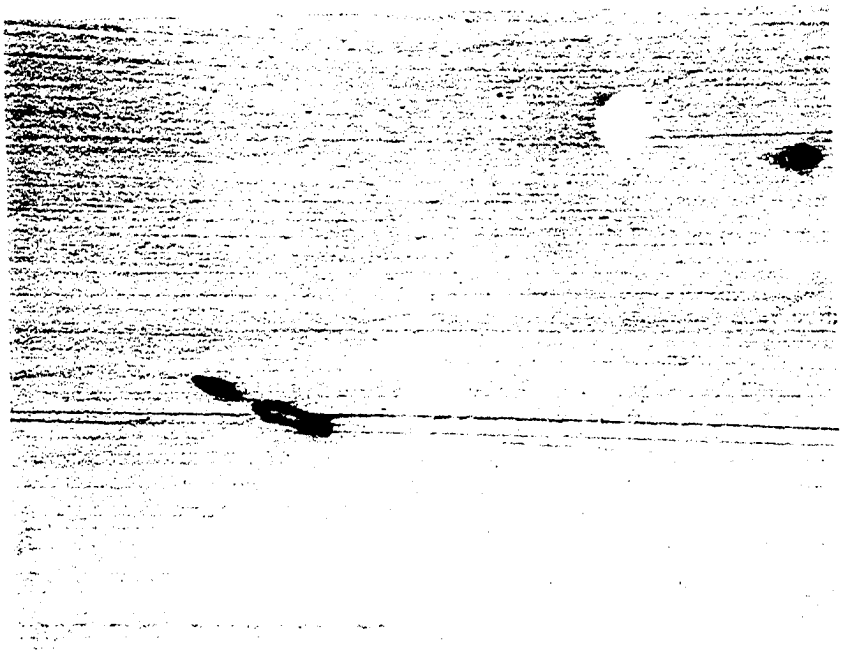

Figure 1. $La_5Pb_3$ I, mechanical polish, air etch. Dark spots--voids, light spots--probably La-$La_5Pb_3$ eutectic. X 250

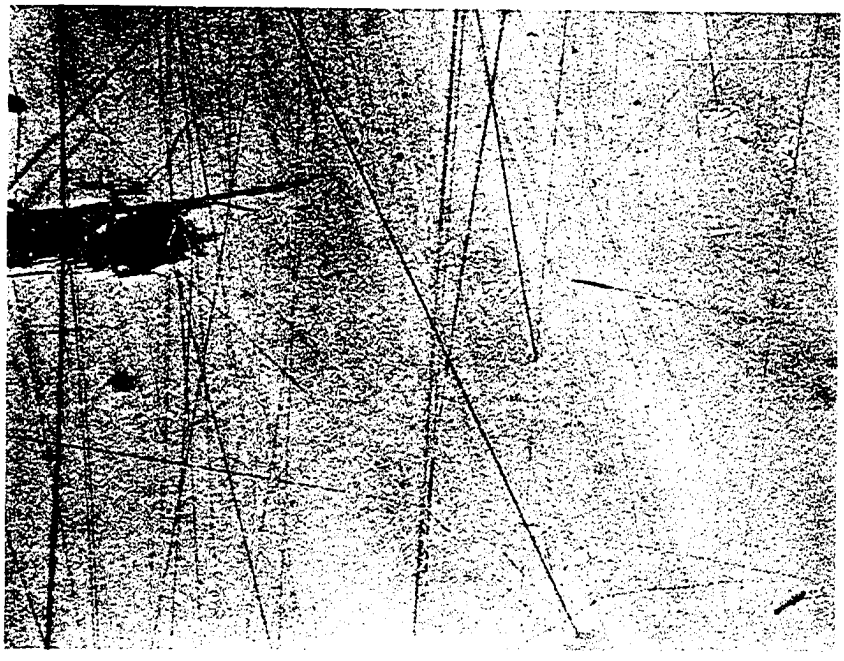

Figure 2. $La_5Pb_3$ II, mechanical polish, air etch. Dark spots--voids, light spots--probably La-$La_5Pb_3$ eutectic. X250

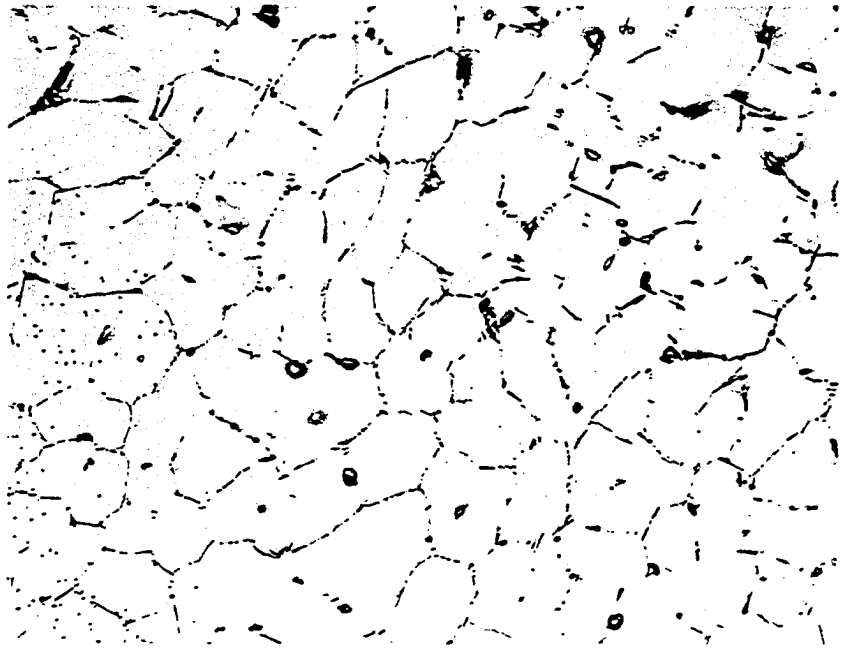

Figure 3. $LaPb_3$, electropolished. Small spots--probably Pb. X250

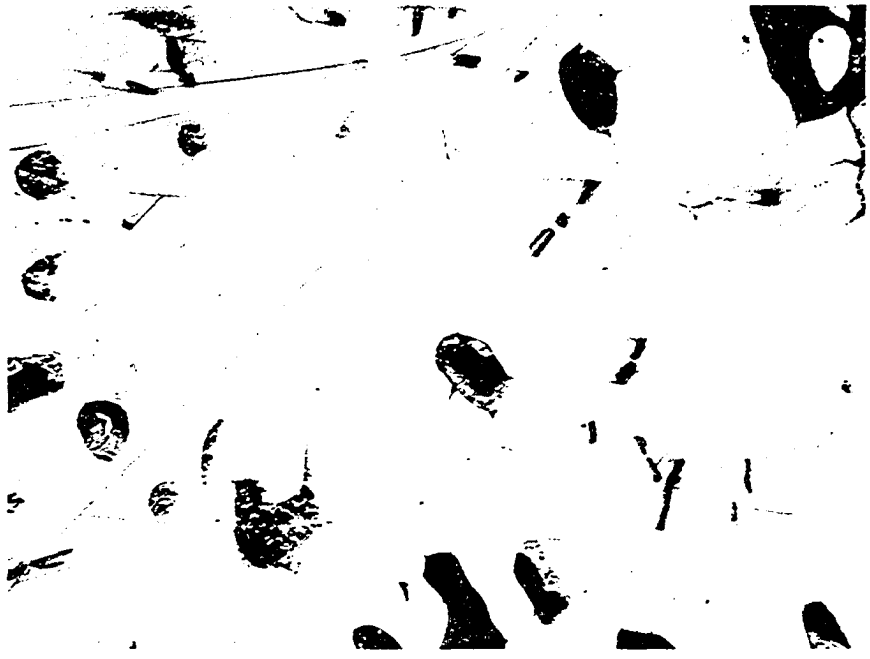

Figure 4. $YPb_3$, mechanical polish, air etch. Small dark grey spots--probably $YPb_2$, large black spots--voids. X250

temperature and its temperature dependence might be unusual, it was thought this might be associated with the vacancy in the 2b positions. Initial attempts were made to add sufficient copper to fill these two sites because Hohnke and Parthé (31) had reported rare earth-bismuth-copper compounds. Metallographic data indicated that only 60% of the copper was taken up by the $La_5Pb_3$ compound (i.e., $La_5Pb_3Cu_{0.6}$) and the excess copper formed a second phase. The lattice parameters reported for the rare earth-bismuth compounds are smaller than the lattice parameters for the rare earth-lead compounds and thus it seems likely that Hohnke and Parthé (31) actually prepared the 5:3:X(X<1) rare earth-bismuth-copper compounds. The addition of carbon was tried next and metallographic data indicated that all the carbon to make $La_5Pb_3C$ is taken up by $La_5Pb_3$ and no second phase material was present in the sample. The $La_5Pb_3C$ compound was prepared in much the same manner as $La_5Pb_3$. The difference was that during the last cooling process the temperature was lowered in 20 C increments from 1510 C, the melting point, to approximately 1200 C. This procedure was followed because the differential thermal analysis used to determine the melting point suggested one or two transitions between 1500 C and 1200 C before the sample was homogenized. The microstructure is shown in Figure 5.

All the samples reacted rapidly with the atmosphere although the samples with the 1:3 structure reacted less rapidly than the samples with the 5:3 structure. Hohnke and Parthé noted that the bismuthides with copper in the 2b holes were more stable than those without the copper. In fact the addition of copper stabilized some lattices that would not form

Figure 5. $La_5Pb_3C$, mechanical polish, air etch. Photomicrograph taken through glass and methyl alcohol. The surface texture is the reaction of the sample with the alcohol. Large dark spots are pits in the surface. X250

unless copper was present. Here, the increase in the melting point for the 5:3:1 compound (1510 C) over the 5:3 compound (1450 C) shows that carbon also stabilizes the structure. However, it does not appreciably reduce the rate at which the atmosphere attacks the samples. As with the bismuthides the addition of copper to the rare earth-lead compounds did reduce the rate of oxidation. The samples were brittle and to get them out of their crucibles both ends of the crucible were cut off and then the tantalum was cut with a jeweler's saw along the entire length of the crucible. The remaining tantalum was peeled away from the sample. The processes of getting the sample out of the crucible, weighing the sample, and mounting the sample in the calorimeter addenda were performed in a helium filled drybox. The sample and addenda were then carried to the calorimeter in a helium filled, sealed jar. Mounting the sample and addenda in the calorimeter had to be done in the room atmosphere, but this took only five minutes or less and the reaction of the samples with the atmosphere was kept to a minimum.

The lattice parameters for the compounds prepared in this investigation are listed in Table 2 along with a summary of data from this and previous investigations. It is interesting to note that the addition of carbon to the lattice causes the c parameter to increase slightly (.023 Å) whereas the work on the bismuthides quoted above showed that copper caused the a parameter to increase (.083 Å).

Table 2. Data available for $YPb_3$, $LaPb_3$, $La_5Pb_3$ and $La_5Pb_3C$

| Compound | $YPb_3$ | $LaPb_3$ | $La_5Pb_3$ | $La_5Pb_3C$ |
|---|---|---|---|---|
| Melting point (°C) | 740[2] | 1160[5] | 1450[5] | 1510 |
| Crystal structure | Cubic<br>$Cu_3Au$<br>$L1_2$ | Cubic<br>$Cu_3Au$<br>$L1_2$ | Hex.<br>$Mn_5Si_3$<br>$D8_8$ | Hex.<br>$Hf_5Sn_3Cu$<br>Filled $D8_8$ |
| Lattice parameters (Å) | $a_o$ = 4.8204 ± 0.0002 A | $a_o$ = 4.9028 ± 0.0002 A | $a_o$ = 9.532 ± .002<br>$c_o$ = 6.974 ± .003 | $a_o$ = 9.531 ± .003<br>$c_o$ = 6.997 ± .002 |
| $\gamma$(mJ/g at.-°$K^2$) | 2.32 ± .77 | 3.25[27] | 0.81 ± .55 | 1.53 ± .31 |
| $\Theta_D^o$(K) | 121 | 147[27] | 150 | 181 |
| $T_s$(K) | 4.6(4.7 ± .09[29]) | 4.1 | -- | -- |
| Magnetic susceptibility $\chi$($cm^3$/g) | 0.11 x $10^{-6}$[29] | 0.165 x $10^{-6}$[29] | -- | -- |
| Thermoelectric power, S(μV/°C) | 4.2[29] | 1.4[29] | -- | -- |
| Resistivity at R.T. (μΩ-cm) | 45 | 49 | 300 | 270 |

## EQUIPMENT AND DATA ANALYSIS

The calorimeter used in this investigation is an adiabatic, pulse type and is described in detail elsewhere (34,35). The sample holder consists of two gold-plated copper plates held together by three gold-plated copper bolts. The samples were smeared with a low vapor pressure grease and mounted between the plates. Temperatures were measured using a Solition germanium resistance thermometer which was calibrated against another germanium resistance thermometer, GR618. GR618 was callbrated against a constant volume gas thermometer (36) and then was used to calibrate other germanium resistance thermometers at Iowa State University. A 1965 Calorimetry Conference Copper Standard (37) was used to check the accuracy of the calorimeter and it was found to be within one percent of the literature values for this standard. The precision of the copper standard was within approximately one percent, but precision of the data taken on the rare earth-lead samples studied in this investigation was not that good. Part of the problem was due to the difference in size of the standard and the samples. The copper standard weighted approximately 66 g while the samples varied in mass from about 10 to 30 g. This means that any uncertainty in the heat capacity of the addenda was increased and contributed to the problem described in the next paragraph.

The data was originally analyzed by the extrapolation of the temperature vs time curves before and after each heat pulse as described by Joseph (35) with the additional specification that a period of approximately four minutes is allowed to lapse after the heat pulse to start the

extrapolation (38) to determine the mid-point temperature of the heat pulse. The waiting period was to allow the sample and addenda to come to equilibrium. It turned out, however, that this waiting period produced extrapolated temperatures that were lower than they were if the extrapolation procedures were begun right after the heat pulse. This problem was magnified because the resistance of the thermometer changes exponentially with temperature but the extrapolation procedure assumes it to be essentially linear. The solution was to start the extrapolation immediately after the heat pulse to find the mid-point temperature for the data points below about 5-7 K (depending on the size of the sample), and to use smaller heat pulses so that the time for the sample to come to equilibrium would be kept to a minimum. This revised procedure was checked by running pulses of different sizes. The size of the pulse did not make any difference in the results as long as it was kept to a minute or less. Furthermore, the data obtained by the old method of determining the mid-point temperatures resulted in considerable scatter of the data points in the C/T vs $T^2$ plot. The revised method yielded C/T vs $T^2$ plots with considerably less scatter. This solution did not provide the most desirable precision but did allow for the data to be analyzed successfully. The points above the 5-7 K range were found to require the usual equilibration time and were handled in the manner described first above.

The $La_5Pb_3C$ sample was the last sample investigated and it was mounted in the addenda two different ways to see if the precision and accuracy of the data could be improved. The first way was as described above and the second way was to wrap the sample in copper foil and grease

to speed up temperature equilibration in the sample. The scatter in the data was less when wrapped with foil and these are the data reported in the results section.

After the heat capacities had been measured portions of the heat capacity samples were used in resistivity measurements. To do this a special holder was constructed to be used with existing resistivity equipment. It was built so that small pieces of the brittle samples could be measured without extensive sawing, cutting or filing which cause the samples to break in small pieces. Spark cutting, normally used for cutting brittle samples to desired shapes, is done in an oil that reacts rapidly with all the lanthanide-lead alloys.

The holder designed was of the four probe type with space to accommodate samples with maximum dimensions of 1.26 cm long, 0.32 cm high and 0.64 cm wide. The samples measured had dimensions that varied from 0.32 cm to 0.64 cm in width and 0.16 to 0.32 cm in height. The distance between voltage probes was 0.32 cm and the distance between current probes was 0.64 cm. Resistances were measured at 4.2 K, 78 K, and room temperature (~ 295 K). The accuracy of the measurements is limited by the lack of uniformity in the dimensions of the samples and the results could be expected to be only within 10 or 20 percent of the true value.

# RESULTS

## $YPb_3$

The heat capacity data from 2.7 to 19.3 K in the form C/T vs $T^2$ are plotted in Figure 6. A least squares fit of the data between 4.7 and 5.9 K gave values of 2.32 $\pm$ .77 mJ/g at. $K^2$ for $\gamma$ and 1.09 $\pm$ .03 mJ/g at. $K^4$ for $\beta$ which gives 121 $\pm$ 1 K for $\Theta_D$. The narrow range for the fit is caused by a small change in slope at about 6 K. Fitting data above this range produced $\gamma$'s that decreased and became negative as more points were included in the fit. The superconducting transition temperature found here was between 4.55 and 4.7 K while Havinga et al. (29) quoted 4.72 $\pm$ .09 K. The variation of the Debye temperature as a function temperature was determined by assuming $C_l = C - \gamma T$, and determining $\Theta_D$ from tables (30) of $\Theta_D/T$ vs C/3R. The effective Debye characteristic temperature, $\Theta_D^{eff}$, decreased from 121 K at 5 K to 119 K at 9 K and then rose to 123 K at 19 K (Figure 7). This general shape is the same as those found for the other compounds studied in this investigation but the magnitude between the minimum and maximum points in the curve is quite different (see Figure 7). The heat capacity versus temperature data are tabulated in the Appendix in Table A(1).

## $LaPb_3$

The heat capacity of $LaPb_3$ was measured from 2.5 K to 20 K. The results are plotted in Figure 8 as C/T vs $T^2$, and are listed in Table A(2) in the Appendix. The superconducting transition temperature, $T_S$, was found to be between 4.12 and 4.18 K in good agreement with previous work

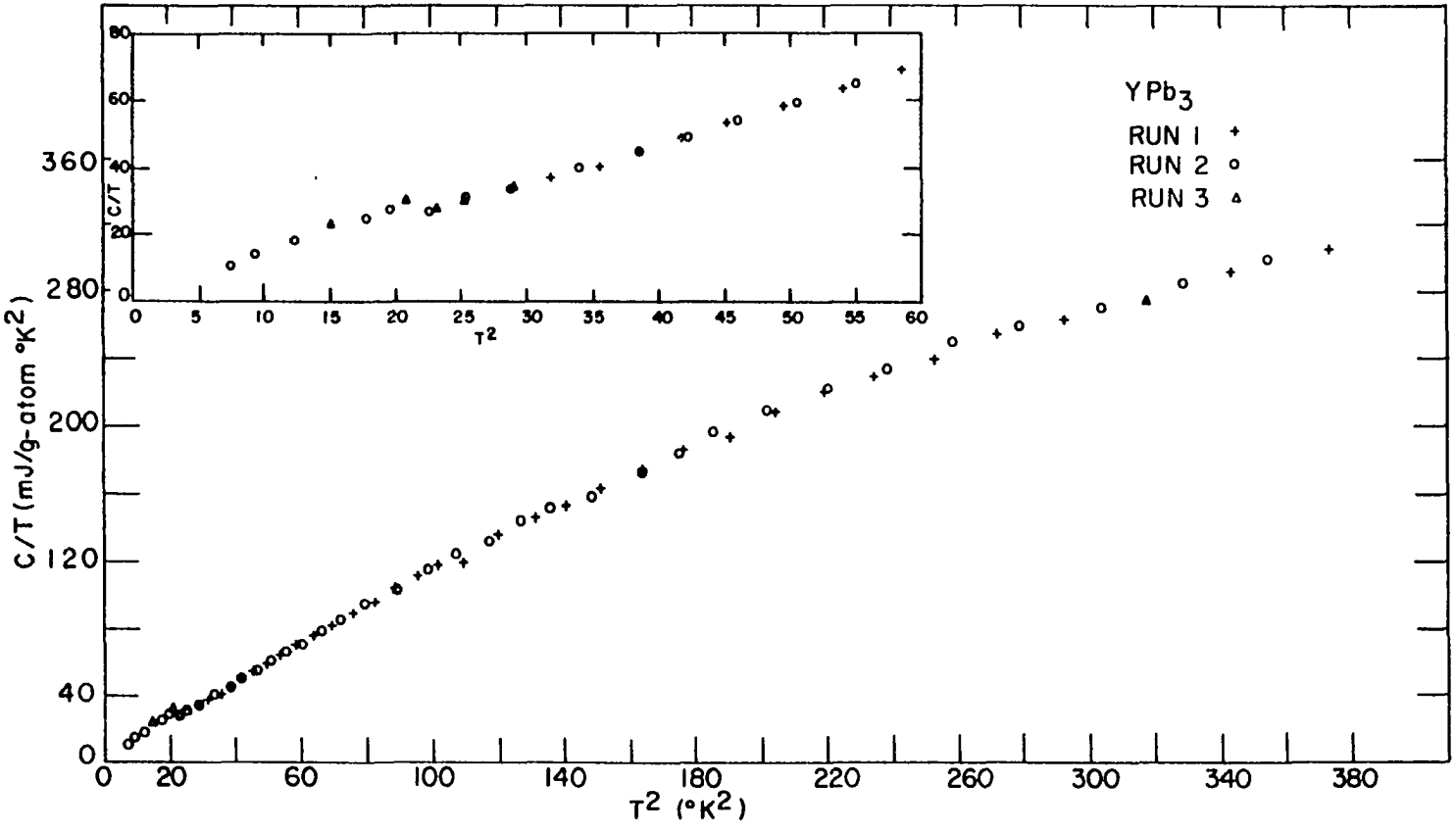


Figure 6. Heat capacity of $YPb_3$ from 2.7 to 19.3 K

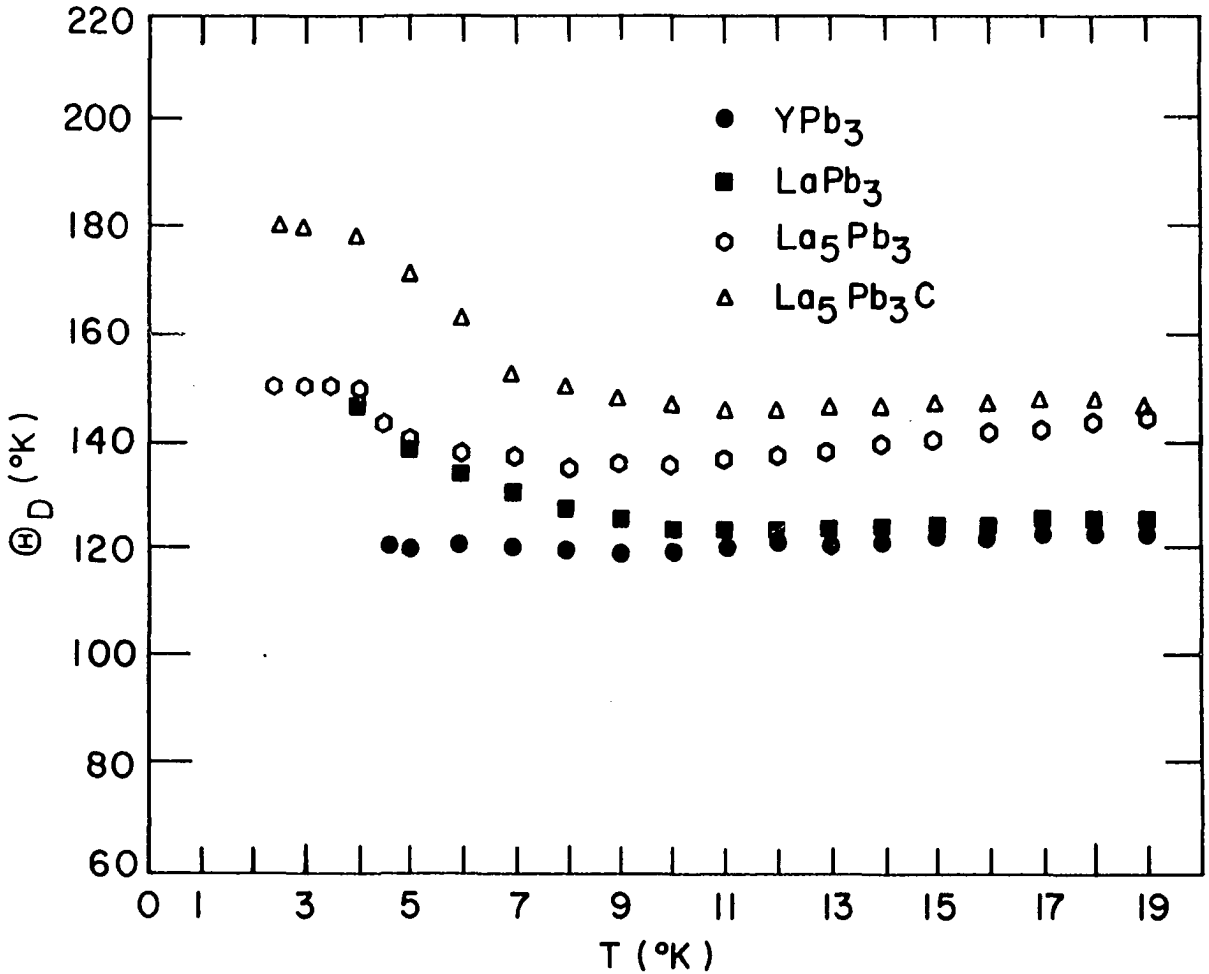


Figure 7. Effective Debye temperature from 2.5 to 20 K for $YPb_3$, $LaPb_3$, $La_5Pb_3$ and $La_5Pb_3C$

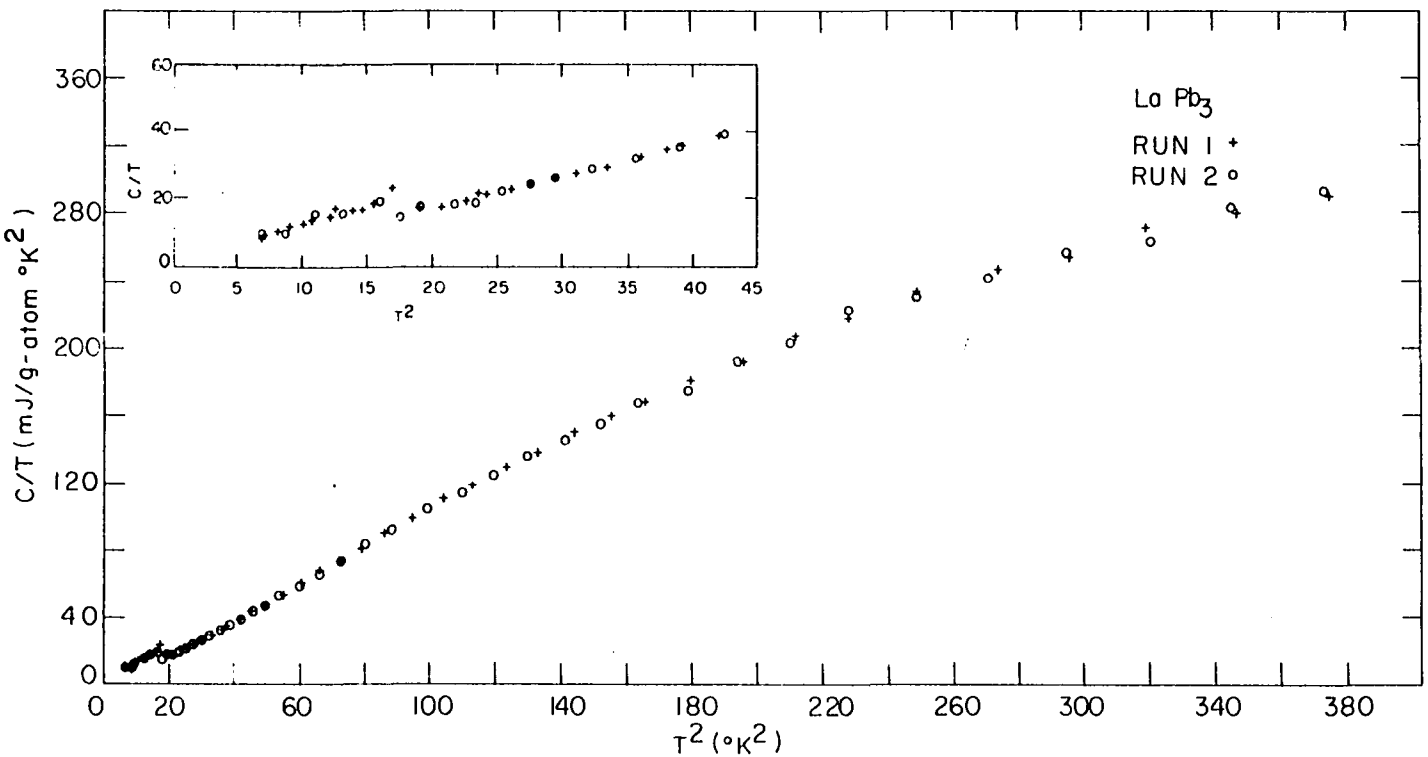


Figure 8. Heat capacity of $LaPb_3$ from 2.6 to 19.4 K

(27-29). Bucher et al. (27) measured the heat capacity at low temperatures in a magnetic field that was sufficient to suppress the superconducting transition temperature. Their results for $\gamma$ and $\Theta_D$ were 3.25 mJ/g at. $K^2$ and 147 K, respectively. If the data (either ours or theirs) above $T_s$ had been used to find $\gamma$ and $\Theta$ it would have yielded values of $\gamma \approx \sim -0.6$ mJ/g at. $K^2$ and $\Theta_D \cong 122$ K. $\Theta_D^{eff}$ was found in the same manner as described for $YPb_3$ and the values are plotted against T in Figure 7. The $\Theta_D^{eff}$ varies from a value of 147 K at 4 K to a minimum of 124 K at about 12 K.

$La_5Pb_3$

The C/T vs $T^2$ data for two $La_5Pb_3$ samples are shown in Figure 9 and the C vs T data are listed in the Appendix in Tables A(3) and A(4). Two samples were prepared because the data for the first one, $La_5Pb_3$ I, showed a considerable amount of scatter below 4 K and it was hoped that the data from the second sample, $La_5Pb_3$ II, might clarify the situation. Elimination of the scatter was quite important because the extrapolation of data above 4 K gives a negative $\gamma$. Once the scatter problem had been solved as described above data from both samples coincided. After the data was reanalyzed a least squares fit (from 2.5 to 3.9 K) gives $\gamma = 0.81 \pm .55$ mJ/g at. $K^2$, $\beta = 0.574 \pm .049$ mJ/g at. $K^4$ and $\Theta_D = 150 \pm 5$ K. The $\Theta_D^{eff}$ vs T plot shows that $\Theta_D^{eff}$ decreases from 150 K to a minimum of 136 K at 8 K and then rises to 145 K at 19 K.

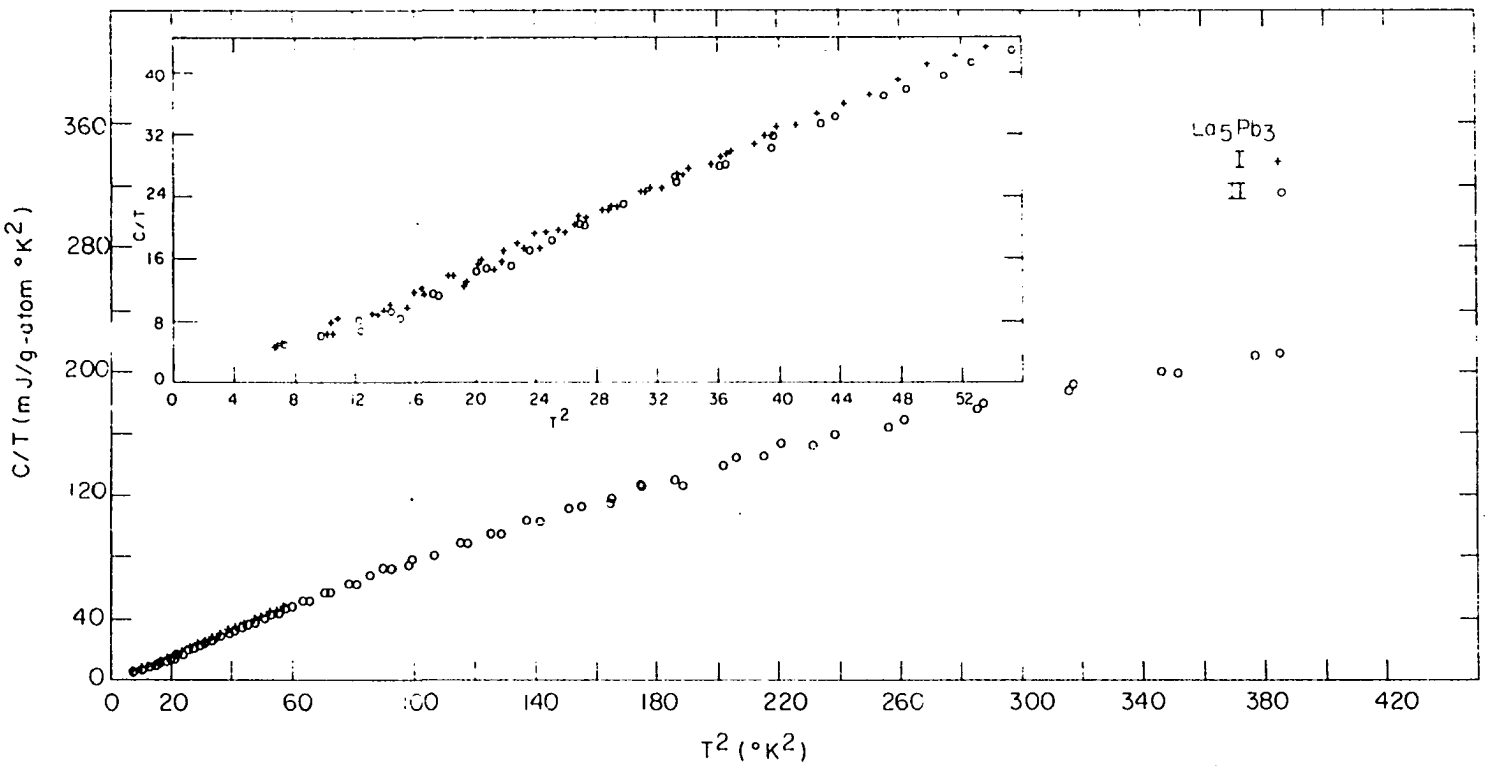


Figure 9. Heat capacity of $La_5Pb_3$ from 2.5 to 19.6 K

### $La_5Pb_3C$

As noted in the section on Equipment and Data Analysis, this sample was measured twice. The second run, which resulted in data with significantly less scatter than the first run, was made with the sample wrapped in copper foil. This is consistent with the resistivity results, which show that the resistivity is higher for this compound than it is for the other compounds at 4.2 K (see the next section). Normally in metals the thermal conductivity is proportional to the electrical conductivity and if that is the case here it would explain the improved results with the sample wrapped in copper.

The heat capacity data are presented in Figure 10 (and in Table A(5) in the Appendix) in the form C/T vs $T^2$. The break in slope for $La_5Pb_3C$ occurs at a higher value of $T^2$ than it does for $La_5Pb_3$. The results from the least squares fit of the data between 2.5 and 4.3 K are $\gamma = 1.53 \pm .31$ mJ/g at. $K^2$ and $\beta = 0.328 \pm .024$ mJ/g at. $K^4$ which gives $\Theta_D^o = 181 \pm 4$ K. The data are also presented as $\Theta_D^{eff}$ vs T in Figure 7.

### Electrical Resistivities

The room temperature resistivities measured for the compounds were 45, 49, 300 and 270 μΩ-cm for $YPb_3$, $LaPb_3$, $La_5Pb_3$, and $La_5Pb_3C$, respectively. With the error in measurements being at least 10% the resistivity values for the $LaPb_3$ and $YPb_3$ compounds can be considered to be about the same. The same can be said for the 5:3 and 5:3:1 compounds. It is reasonable to say that the resistivity for the 1:3 compounds is about 1/6 of the resistivity for the 5:3 and 5:3:1 compounds. The temperature dependence of the electrical resistivity is best illustrated by a plot of

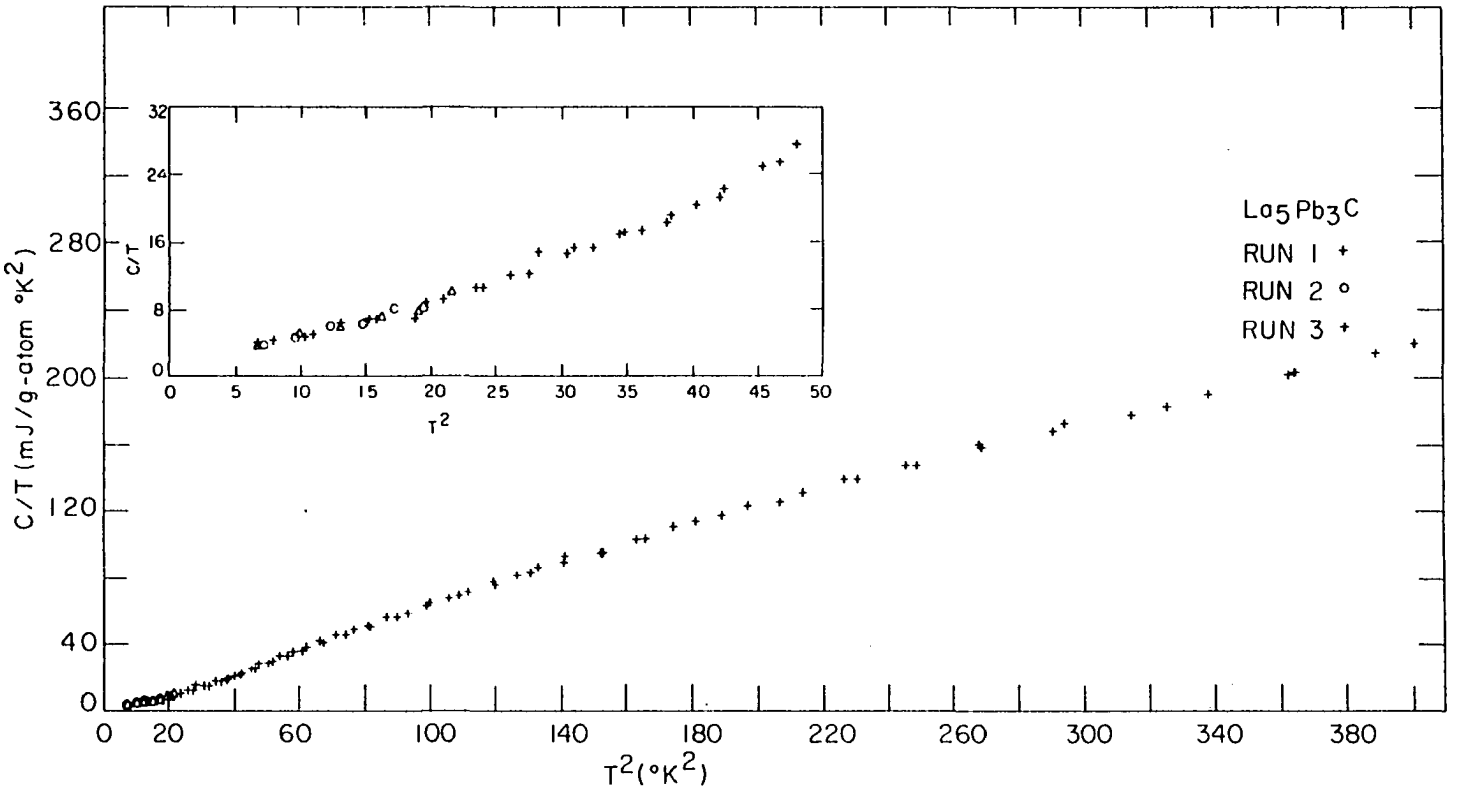


Figure 10. Heat capacity of $La_5Pb_3C$ from 2.5 to 20 K

the reduced resistivity or $\rho_T/\rho_{295}$ against the temperature, Figure 11. It is noted that the values for $YPb_3$, $LaPb_3$, and $La_5Pb_3$ decrease rapidly with temperature in a manner expected for normal metallic conductors, while the values for $La_5Pb_3C$ decrease quite slowly. This will be discussed later.

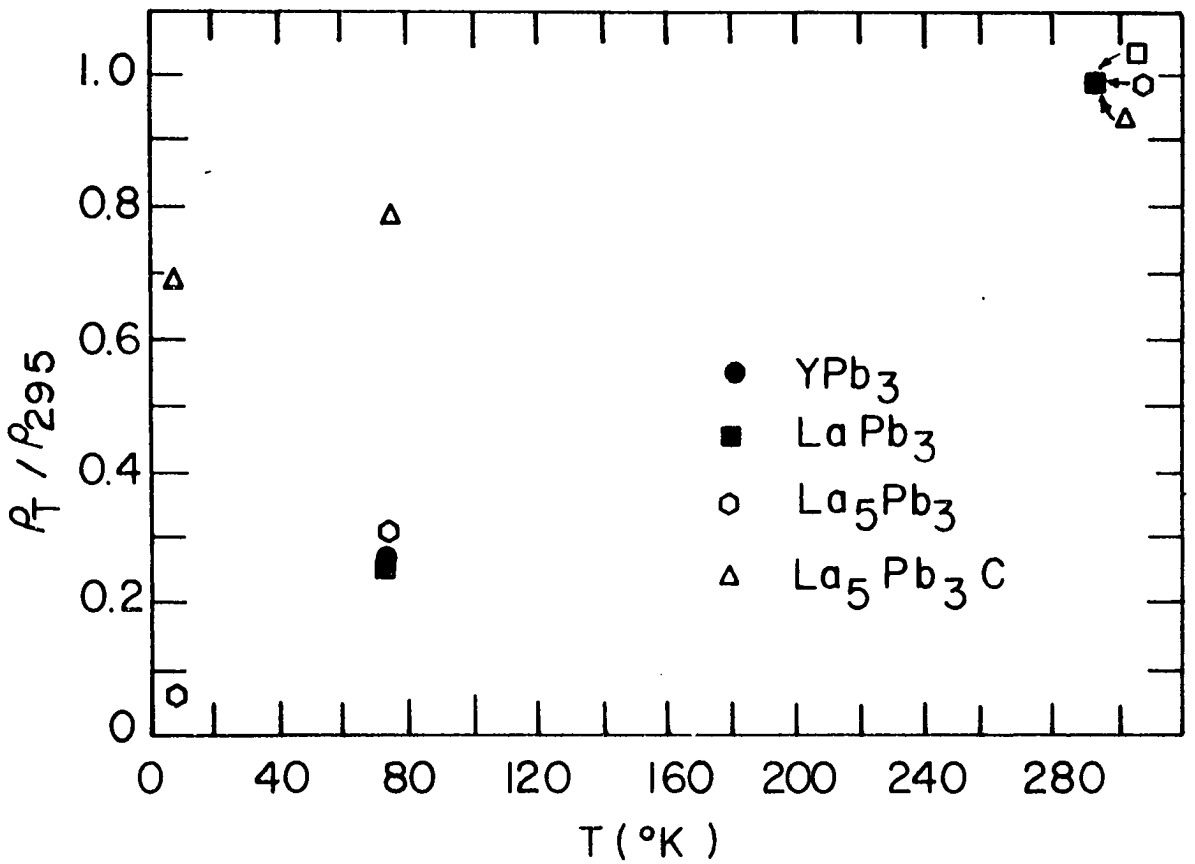


Figure 11. Reduced resistivities for $YPb_3$, $LaPb_3$, $La_5Pb_3$ and $La_5Pb_3C$ at 4.2, 78 and ~ 295 K

# DISCUSSION

The lanthanum compounds studied in this investigation all deviate from Debye behavior at low temperatures as shown by the C/T vs $T^2$ curves. This presents problems both for the fitting of the curves and for using this data to predict how the rest of the rare earth-lead compounds will behave. In the following paragraphs the numbers obtained here will be compared with each other and with other data to see if they are consistent. Different models and methods of fitting the data will be used to achieve this end and also to see if the data obtained here will allow predictions about the magnitude of the properties of the other lanthanide-lead compounds.

## Electronic Specific Heat Coefficients

There has been no heat capacity work for the 5:3 and 5:3:1 compounds in the lanthanide-lead systems and very little on the 1:3 compounds. Thus there is only a limited amount of information that can be used to cross check the results of this investigation.

Bucher *et al.* (27) measured the heat capacity for $LaPb_3$ both in the normal state and the superconducting state and showed that there was a change in the slope of the C/T vs $T^2$ curve at the superconducting transition temperature. Normally the slope of the curve stays constant above and below $T_s$ when the heat capacity is measured in the normal state (30,35). The normal state data below $T_s$ for $LaPb_3$ give a positive $\gamma$ but that above $T_s$ give a negative $\gamma$ value, which is a physical impossibility. The data between the transition temperature and the first change in slope for

$YPb_3$ produce a positive $\gamma$. If the data above that first change in slope are used then the extrapolation to 0°K produces a negative $\gamma$ as in the $LaPb_3$ compound. If data were taken for $YPb_3$ in the normal state below $T_s$ then it is possible that there is another change in slope that occurs which would give both a different $\gamma$ and a different $\theta_D$.

To see if the $\gamma$ values for these two compounds, $YPb_3$ and $LaPb_3$, are reasonable it is possible to use some of the data that Havinga et al. (29) have published. They measured the superconducting transition temperatures, the thermoelectric power and the susceptibilities of these two compounds. Both of the compounds are weak paramagnets and since the magnetic susceptibility for these kind of materials is proportional to the density of states at the Fermi energy as is the electronic specific heat constant one can check to see if the data are consistent with one another. The ratio of the susceptibilities (see Table 2) is 1:5 which compares very favorably to the ratio of the $\gamma$ values (1.4). Thus these ratios lend credibility to the $\gamma$ value found in this investigation for $YPb_3$.

Another parameter which also supports the $\gamma$ value for $YPb_3$ is the ratio $\Delta C/\gamma T_s$ where $\Delta C$ is the change of heat capacity at $T_s$, and $\gamma$ and $T_s$, are defined as above. According to BCS theory the above relation should be equal to 1.52. Experimentally it was found that $\Delta C/\gamma T_s$ equaled 2.16 and 1.97 for $YPb_3$ and $LaPb_3$ respectively. Again the closeness of these values indicates the $\gamma$ value for $YPb_3$ is reasonable. These $\Delta C/\gamma T_s$ values are higher than values reported by Joseph et al. (39) and Hungsberg and Gschneidner (40) for other rare earth intermetallic compounds which had

values equal to or lower than the BCS theoretical value of 1.52. Assuming that the data obtained for $YPb_3$ are correct the $\gamma$ values for the rest of the rare earth-lead 1:3 compounds should be expected to be less than or approximately equal to 3mJ/g at. $K^2$.

The $\gamma$ values for $La_5Pb_3$ and $La_5Pb_3C$ are both small, and within the experimental error limits they are the same. Although the effect of adding carbon to $La_5Pb_3$ appears to increase the density of states at the Fermi surface, the lack of precision prevents one from stating this conclusively. Before the problem with the data analysis was solved it appeared that these two compounds would have $\gamma$ values $\simeq 0$ and thus might be semiconductors or semimetals. The resistivity measurements and also the $\gamma$ values given herein, show that they are metallic materials with unfilled valence bands.

## Lattice Heat Capacity

The Debye theory is based on the assumption that the vibrations of the lattice at low temperatures have a distribution, $g(\nu)$, which is proportional to the vibrational frequency squared, $\nu^2$. Unfortunately, as many heat capacity experiments have shown, this particular model fails because the distribution of vibrational modes $[g(\nu)]$ is not a smooth function of the frequency up to $\nu_{max}$, but has some peaks and valleys. Normally, however, the model is found to hold in the low temperature range below $\Theta_D^o/30$.

For all four of the compounds investigated here a deviation from this model has been found, but fortunately there is a portion of the C/T vs $T^2$ plot which provides a straight line so that a least squares fit can be

made and a value for the limiting Debye characteristic temperature, $\Theta_D^o$, can be calculated.

Lindemann proposed a relation (41)

$$[\Theta_D = k\left(\frac{T}{V^{2/3}_M}\right)^{1/2}]$$

which takes into account the melting point of the compound or element, T, the mass per mole for elements or g at. for alloys, M, the volume per g at., V, and the Debye temperature, $\Theta_D$, and for compounds that are isostructural the constant of proportionality, k, should be the same. There is another relation which can be used to compare $\Theta_D$ values but it does not take into account the melting point and molecular volume of the compound but does take into account the difference in mass between two compounds. This relation says that the product of $\Theta_D$ and the square root of the mass should be constant for isostructural compounds. Table 3 lists the values for the proportionality constant for the Lindemann relation and the product $\Theta_D^o\sqrt{M}$ .

As can be seen from Table 3 the values of k for $LaPb_3$ and $YPb_3$ (165 and 154, respectively) differ as much as might be expected for these similar compounds. Perhaps the large difference in melting points (740 K-$YPb_3$ and 1160 K-$LaPb_3$) and the mode of melting ($YPb_3$ melts incongruently and $LaPb_3$ melts congruently) account for this 8% difference. Even though these relations show that there seems to be large differences between the product $\Theta_D^o\sqrt{M}$ using the Debye temperature from the low temperature slope of the C/T vs $T^2$ plot, the $\Theta_D^{eff}$ vs T plot (Figure 7) shows that $LaPb_3$ and $YPb_3$ have almost the same Debye temperature at temperatures

Table 3. Comparison of the compounds using standard relations

| Compound | Mass/Mole | Mass/g at. | $\sqrt{M}$ | $\Theta_D^o$ | $\Theta_D^o\sqrt{M}$ | $k_{Lindemann}$ |
|---|---|---|---|---|---|---|
| $YPb_3$ | 710 | 178 | 13.34 | 121 | 1609 | 154 |
| $LaPb_3$ | 760 | 190 | 13.79 | 147 | 2027 | 165 |
| $La_5Pb_3$ | 1316 | 164 | 12.82 | 151 | 1935 | 191 |
| $La_5Pb_3C$ | 1328 | 148 | 12.14 | 180 | 2197 | 205 |

above 12K. Thus when the product of $\Theta_D^{eff}\sqrt{M}$ from the higher temperature region is used the values have a difference of only 9% whereas the low temperature values of $\Theta_D^{o}\sqrt{M}$ differ by about 25%. In the Lindemann relation the agreement is enough better that it indicates that the melting point of the compounds should not be overlooked when comparing Debye temperatures of closely related solids. Both of these relations give reasonable confirmation to the calculated $\Theta_D^{o}$ for $YPb_3$.

Using these two relations to compare the Debye temperatures for the 5:3 and 5:3:1 compounds probably is not good practice because there is a difference in the structures. In the 5:3:1 compound with the carbon in the "holes" the vibrational distribution would be expected to be different than that for the 5:3 compound and the Debye temperature would also be different. There is a difference in the Debye temperatures from the straight portion of the C/T vs $T^2$ curves, but the plot of effective Debye temperatures (Figure 7) shows that at 20 K the two lattices have the same $\Theta_D^{eff}$. Also the general shape of the two curves is different. Where the $La_5Pb_3$ curve has a definite minimum and begins to increase again, the $La_5Pb_3C$ compound has a $\Theta_D^{eff}$ curve that drops from a high value at low temperatures to a lower value and then stays constant throughout the temperature range investigated. The Lindemann constants for the two compounds with the $D8_8$ structure do not agree and neither do the products of the Debye temperature times the square root of the mass. The differences are 7% and 12% respectively, which is less than the differences for the two $AuCu_3$ type structures. However, one might have expected the differences for the $AuCu_3$ structures to be less.

The deviations of the effective Debye temperatures from a horizontal line (Figure 7) indicate that the Debye approximation does not hold with the exception, perhaps, of the $YPb_3$ lattice. The fit for $YPb_3$ may deviate if the heat capacity measurements would be taken at temperatures lower and higher than measured here. Knowing that the Debye approximation does not work the logical approach was to see if there would be some model that would fit the temperature dependence of the specific heats for the $La_5Pb_3$ and $La_5Pb_3C$ compounds.

Because the lanthanum atoms in the 4d positions are closer together than their normal metallic state it was thought that a model originally proposed by Tarassov and successfully applied by deSorbo (42) to antimony, selenium and tellurium might fit the heat capacities for the 5:3 and 5:3:1 compounds. Basically Tarassov suggested that if layers of a structure were further apart than the atoms within a layer then the lattice contribution of the specific heat could be expressed as a sum of two terms. The first would be a two-dimensional Debye lattice for the vibrations within the layers or planes and the second would be a three dimensional Debye lattice for the interlayer vibrations. For a solid which contains a chain of atoms and where spacing between chains and spacing within chains varies, he suggested that the lattice contribution consisted of the sum of a one dimensional and a three dimensional Debye lattice. Thus for both kinds of solids two vibrational frequencies or effective characteristic temperatures were needed to explain the lattice heat capacities. Because there is the change in slope in the $C/T$ vs $T^2$ plots for both $D8_8$ compounds it was felt that the low temperature data might represent one

vibrational frequency while the higher temperature data would represent the sum of the two frequencies.

In these cases both of Tarassov's models were tried. First the one with the one dimensional chains was tried because of the spacing between the atoms in the 4d sites, which form chains in the $D8_8$ compounds and then the model for the two dimensional layers was tried because the vibrations in the basal plane and the plane parallel to the basal plane at Z = 1/2 might be affected by the holes at the corners of the unit cells. Neither one worked. Any combination of the two vibrational frequencies that fit at low temperatures did very poorly at fitting the higher temperature data.

Further trials were carried out by using simple combinations of Einstein and Debye functions but these also failed. The same problem arose when fitting the heat capacity results by a power series equation, $C = AT + BT^2 + CT^3 \ldots$ The higher temperature portion was fitted quite well but the errors for the points below the slope change (in the C/T vs $T^2$) plots were too large to be acceptable. For example the $La_5Pb_3C$ data would fit within 2% for the temperatures above 5.5 K but the data below 5.5 K deviated from the fit by as much as 13%.

Because the various models did not work successfully and because the curves of $\Theta_D^{eff}$ vs T did not reveal more than the fact that the lanthanum-lead compounds did not follow the Debye approximation which the $YPb_3$ compound apparently came rather close to fitting, it was decided to try to treat the heat capacity data a different way.

Bijl (43) proposed another way of representing heat capacity data

because he felt that the effective Debye temperature plotted against T was not revealing much about the similarities and differences in different lattices. Most of his objections were for temperatures higher than the range covered here, but two of them were pertinent at all temperatures. The first is that presenting the data as a function of T rather than as a function of some reduced form of T, such as $T/\Theta_D^o$, does not allow compounds to be compared to each other. This objection can be dealt with easily by plotting $\Theta_D^{eff}$ as a function of $T/\Theta_D^o$. Some researchers do this but the standard form still seems to be $\Theta_D^{eff}$ vs T. He feels that his second objection is more important. Bijl found that fitting the data using the method described in the Results Section ($C - \gamma T = C_{lattice}$, then finding $\Theta_D^{eff}$ from the tables) produced curves of $\Theta_D^{eff}$ vs T in which $\Theta_D^{eff}$ is decreasing while the distribution function, $g(\nu)$, was actually found to be increasing faster than Debye's proposed $g(\nu) \equiv \nu^2$. What he wanted was a method of representing the specific heat data that would show the deviation of $g(\nu) \equiv \nu^2$ directly. Thus if the actual frequency distribution increased faster or slower than the Debye model the new representation should indicate that change directly.

He proposed calculating the Debye characteristic temperature from the low temperature slope of the C/T vs $T^2$ plot, $\Theta_D^o$, and then using this Debye temperature he found a theoretical value for the heat capacity of the lattice, $C_\ell^D$, for every temperature from the tables of $C_{lattice}/3R$ vs $\Theta_D/T$. This gives values of the expected Debye lattice heat capacity. The next step was to find the experimental value of the heat capacity of the lattice, $C_\ell^{exp}$, for the corresponding temperature. The experimental value

of the lattice heat capacity is divided by the theoretical value and the resultant, $C_{reduced}$ or $C_r$, value is plotted against $T/\Theta_D^o$. In this way if the lattice was acting as a Debye lattice at all the temperatures investigated the value of $C_r$ would equal 1.000 at all values of $T/\Theta_D^o$. If the heat capacity of the lattice deviated from the Debye model, such that $g(\nu)$ increased faster or slower than the Debye model would have allowed, $C_r$ would become greater than 1 or less than 1, respectively. The data for the four compounds investigated are shown in Figure 12. Bijl noted in his article that the peak in $C_r$ for most elements was near $T/\Theta_D^o = 0.1$, but as the mass of the element or equivalently the mass per g at. in a compound or alloy become larger the peak in $C_r$ shifted to a lower $T/\Theta_D$ value and became larger. The compounds studied here have peaks in $C_r$ which occur at values of $T/\Theta_D$ ranging from 0.05 to 0.075.

At this point Bijl's observation about where the peak in $C_r$ occurs seems to hold within the particular type of crystal structure, but does not appear to hold between structure types. For the compounds with a larger mass per g at. of the $AuCu_3$ structure type, i.e., $LaPb_3$, a peak in $C_r$ occurs at a lower $T/\theta_D^o$ than the one for $YPb_3$. The same is true for the $La_5Pb_3$ and $La_5Pb_3C$ compounds. Yet the peaks for both $La_5Pb_3$ and $La_5Pb_3C$, which have a smaller mass per g at., are at lower $T/\Theta_D$ than are the 1:3 compounds. His observation that the height of $C_r$ increases as the mass increases holds only for the $AuCu_3$ structures but does not appear to hold for the $D8_8$ and filled $D8_8$ structures. Keep in mind that Bijl developed this representation for the elements and made his observations on the work that had been done up to the time that the paper was written and there

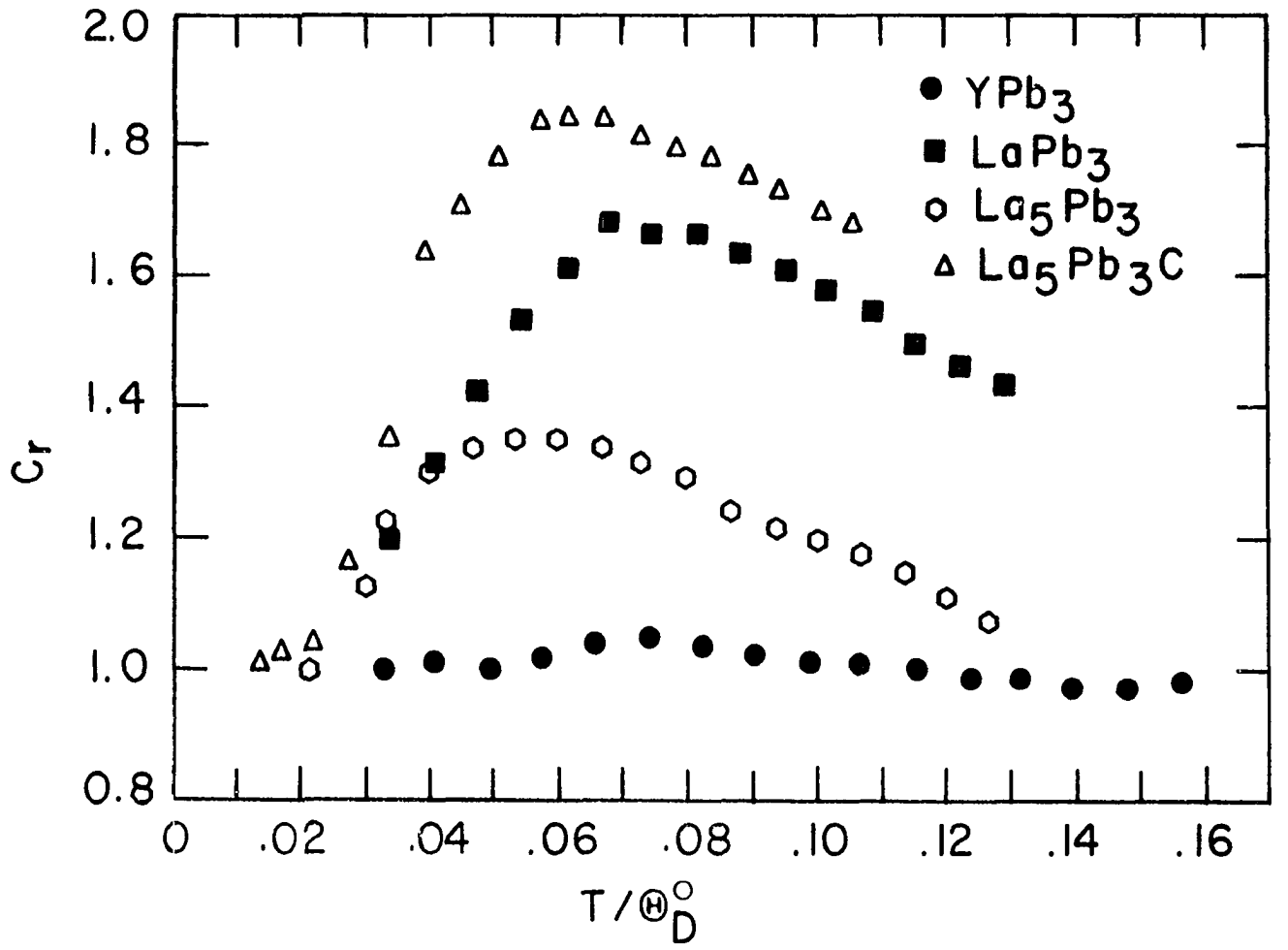


Figure 12. Reduced heat capacity for $YPb_3$, $LaPb_3$, $La_5Pb_3$ and $La_5Pb_3C$ plotted against $T/\Theta_D^o$

were only a few metals investigated that had strongly anisotropic lattices.

Two of the elements that he observed that did have strongly anisotropic lattices were zinc and cadmium. Both of these elements had their peaks shifted to a value of $T/\Theta_D < 0.1$. This was felt to be due to the fact that the waves in the c direction for these elements apparently are excited more easily than the lattice waves in the a direction. Perhaps this is the key to the discrepancies noted above. The $D8_8$ lattice would be more likely to be anisotropic than would the $AuCu_3$ structure types for two reasons which were discussed in the Introduction: (1) the holes in the $D8_8$ structure which affect the vibrations of the atoms surrounding them, and (2) the atoms in the 4d positions which are closer to each other than in their pure metallic state and also closer together than the rest of the atoms in the structure. Therefore if the differences in anisotropy in the two types of lattices investigated here are considered, Bijl's representation and comments seem to be consistent with the exception of his explanations for peak height.

With this representation of the data as with previous calculations there seem to be discrepancies between the $YPb_3$ data and the $LaPb_3$ data. The $YPb_3$ data was almost a straight line while the $LaPb_3$ data had a definite peak. Bijl showed that elements with the same crystal structure and valence had reduced curves that were very similar. To see if this would be true for alloys three lanthanide-aiuminum laves phase compounds, $RAl_2$, were compared using this representation. Hungsberg's data for $YAl_2$, $LaAl_2$ and $LuAl_2$ (44) were put in the reduced form and plotted. Although the

data was not sufficient to determine peak heights, the data for the three compounds fell almost on the same line. When the Lindemann constant for $LaPb_3$ was used to find a $\Theta_D^o$ for $YPb_3$ and this $\Theta_D^o$ was used in a reduced plot it provided a curve with the same shape as the $LaPb_3$ curve although the magnitudes were not as close as those of the $RAl_2$ compounds. The $RAl_2$ data implies that the same situation should hold for other series of compounds. Both $LaPb_3$ and $YPb_3$ are superconductors and the data from these two compounds is to be used to represent the lattice and electronic contributions to the heat capacity of normal trivalent $RPb_3$ alloys. The $LaAl_2$ compound is superconducting but the other two $RAl_2$ are not, yet their reduced curves are nearly the same. The only difference is that the $LaAl_2$ electronic specific heat constant is about twice those of $YAl_2$ and $LuAl_2$. Knowing these facts it is reasonable to say that the lattice contribution from the $LaPb_3$ compound can be used to represent the other $RPb_3$ compounds but to use the $LaPb_3$ $\gamma$ value for the other compounds would be questionable in view of the data for the $RAl_2$ compounds. It would be reasonable to use the $La_5Pb_3$ data to represent the lattice and electronic contributions to the heat capacity for the other trivalent $R_5Pb_3$ alloys.

The reduced form for one compound does appear to give the shape of the curve for the other isostructural compounds. Lindemann's equation based on one compound does give an approximate $\Theta_D^o$ for the other isostructural compounds. Using the two together provides not only what the shape of the lattice contribution should be but a fair estimate of the magnitude of that contribution.

For both types of structures investigated here more information would

be helpful if detailed calculations of the various contributions to the heat capacity of the other lanthanide-lead compounds are to be made. Specifically data from $YPb_3$, in the normal state, would help establish what the effect of changing the mass of the lanthanide element has on the lattice contribution as would the data for $Y_5Pb_3$ and $Lu_5Pb_3$. These data would also provide more information about the usefulness of Bijl's and other reduced representations.

# CONCLUSIONS

This investigation has provided the electronic and lattice contributions to the heat capacity for the 1:3 and 5:3 lanthanide-lead compounds. Work on other compounds in these series would produce more accurate estimates of these contributions for the trivalent lanthanide-lead compounds with magnetic moments. The methods used to compare the results for $YPb_3$ and $LaPb_3$ show that the results for $YPb_3$ are reasonable but any doubt could be dispelled by measuring the heat capacity of $YPb_3$ in the normal state. Fitting the heat capacities with various models proposed by other investigators did not provide any explanations as to how or why the actual distribution of lattice vibrations, $g(\nu)$, varies with the frequency, $(\nu)$. Bijl's reduced representation provides information on the extent of the deviation from Debye's model of the lattice contribution to the heat capacity of alloys but some of the observations of the influence of mass and anisotropy on the lattice contribution of elements do hold for alloys while others do not. Although more investigation is needed his reduced representation apparently shows that isostructural compounds should have reduced lattice heat capacities that are very similar.

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# APPENDIX

Table A(1). Heat capacity of $YPb_3$

| T (deg K) | C (mJ/g-at K) | T (deg K) | C (mJ/g-at K) |
|---|---|---|---|
| 2.744 | 27.76 | 9.777 | 1082.72 |
| 3.045 | 42.83 | 9.959 | 1141.66 |
| 3.505 | 62.34 | 10.081 | 1183.49 |
| 3.886 | 88.58 | 10.365 | 1280.34 |
| 4.212 | 104.06 | 10.478 | 1243.41 |
| 4.429 | 123.45 | 10.848 | 1425.11 |
| 4.562 | 136.70 | 10.968 | 1487.69 |
| 4.746 | 126.51 | 11.277 | 1625.08 |
| 4.800 | 129.93 | 11.459 | 1666.33 |
| 5.022 | 148.61 | 11.664 | 1765.27 |
| 5.034 | 154.01 | 11.858 | 1808.40 |
| 5.365 | 180.47 | 12.192 | 1919.90 |
| 5.386 | 181.72 | 12.298 | 2001.50 |
| 5.640 | 208.66 | 12.813 | 2211.32 |
| 5.827 | 231.23 | 12.814 | 2232.95 |
| 5.958 | 240.77 | 13.237 | 2423.48 |
| 6.209 | 275.36 | 13.275 | 2453.55 |
| 6.211 | 278.52 | 13.638 | 2662.81 |
| 6.464 | 316.44 | 13.802 | 2669.64 |
| 6.499 | 320.18 | 14.224 | 2964.18 |
| 6.723 | 359.16 | 14.303 | 2971.46 |
| 6.789 | 366.10 | 14.817 | 3249.97 |
| 7.045 | 411.07 | 14.854 | 3283.64 |
| 7.112 | 422.62 | 15.314 | 3503.35 |
| 7.353 | 468.01 | 15.456 | 3599.18 |
| 7.420 | 483.19 | 15.906 | 3793.37 |
| 7.658 | 530.37 | 16.086 | 3998.76 |
| 7.771 | 547.08 | 16.500 | 4186.54 |
| 7.987 | 604.22 | 16.711 | 4316.57 |
| 8.135 | 632.08 | 17.120 | 4499.56 |
| 8.332 | 679.35 | 17.449 | 4699.25 |
| 8.504 | 722.44 | 17.837 | 4871.70 |
| 8.708 | 776.00 | 18.142 | 5148.89 |
| 8.915 | 840.03 | 18.537 | 5395.73 |
| 9.074 | 866.25 | 18.834 | 5611.25 |
| 9.437 | 980.81 | 19.325 | 5896.81 |
| 9.446 | 975.66 | | |

Table A (2).. Heat capacity of $LaPb_3$

| T (deg K) | C (mJ/g-at K) | T (deg K) | C (mJ/g-at K) | T (deg K) | C (mJ/g-at K) |
|---|---|---|---|---|---|
| 2.619 | 22.02 | 5.422 | 139.54 | 10.621 | 1260.17 |
| 2.642 | 25.51 | 5.576 | 152.13 | 10.929 | 1351.88 |
| 2.653 | 23.15 | 5.681 | 161.45 | 11.092 | 1431.45 |
| 2.866 | 29.14 | 5.781 | 169.72 | 11.392 | 1542.02 |
| 2.977 | 27.78 | 5.968 | 189.78 | 11.513 | 1584.63 |
| 2.999 | 35.04 | 6.002 | 193.65 | 11.889 | 1731.47 |
| 3.183 | 39.90 | 6.166 | 212.65 | 11.990 | 1791.14 |
| 3.275 | 43.91 | 6.245 | 220.17 | 12.320 | 1908.43 |
| 3.328 | 49.80 | 6.255 | 222.13 | 12.462 | 1977.14 |
| 3.483 | 50.78 | 6.475 | 248.69 | 12.789 | 2123.61 |
| 3.541 | 60.50 | 6.490 | 252.61 | 12.878 | 2160.95 |
| 3.625 | 55.66 | 6.514 | 255.03 | 13.371 | 2331.97 |
| 3.738 | 61.23 | 6.752 | 288.69 | 13.404 | 2418.50 |
| 3.823 | 63.39 | 6.793 | 289.67 | 13.949 | 2664.72 |
| 3.945 | 72.31 | 7.039 | 330.63 | 13.997 | 2679.09 |
| 3.995 | 76.26 | 7.069 | 336.06 | 14.509 | 2926.36 |
| 4.017 | 76.26 | 7.366 | 385.74 | 14.562 | 2999.24 |
| 4.124 | 93.90 | 7.419 | 395.43 | 15.110 | 3334.20 |
| 4.188 | 60.22 | 7.731 | 453.09 | 15.116 | 3271.22 |
| 4.361 | 74.58 | 7.802 | 465.17 | 15.774 | 3609.69 |
| 4.378 | 76.31 | 8.122 | 531.59 | 15.788 | 3659.99 |
| 4.549 | 78.37 | 8.152 | 540.84 | 16.455 | 3952.62 |
| 4.659 | 84.08 | 8.533 | 628.57 | 16.540 | 4066.98 |
| 4.757 | 90.07 | 8.533 | 624.93 | 17.187 | 4384.00 |
| 4.826 | 87.54 | 8.907 | 723.81 | 17.199 | 4347.69 |
| 4.854 | 102.59 | 8.948 | 738.64 | 17.868 | 4826.02 |
| 4.914 | 102.48 | 9.286 | 832.75 | 17.908 | 4681.90 |
| 5.038 | 109.46 | 9.407 | 860.29 | 18.584 | 5245.47 |
| 5.104 | 114.45 | 9.741 | 957.73 | 18.623 | 5191.25 |
| 5.247 | 124.28 | 9.960 | 1030.25 | 19.326 | 5623.10 |
| 5.248 | 125.50 | 10.196 | 1122.89 | 19.365 | 5602.11 |
| 5.418 | 138.32 | 10.478 | 1191.58 | | |

Table A (3). Heat capacity of $La_5Pb_3$ I

| T (deg K) | C (mJ/g-at K) | T (deg K) | C (mJ/g-at K) | T (deg K) | C (mJ/g-at K) |
|---|---|---|---|---|---|
| 2.675 | 11.36 | 6.613 | 226.16 | 11.906 | 1221.23 |
| 2.713 | 13.43 | 6.851 | 251.20 | 12.296 | 1372.21 |
| 3.127 | 18.86 | 6.956 | 261.05 | 12.458 | 1396.79 |
| 3.131 | 18.69 | 7.142 | 279.84 | 12.844 | 1510.05 |
| 3.508 | 27.65 | 7.262 | 298.21 | 12.844 | 1476.03 |
| 3.517 | 22.98 | 7.440 | 317.75 | 13.234 | 1682.02 |
| 3.797 | 34.42 | 7.598 | 348.81 | 13.253 | 1670.25 |
| 3.873 | 31.52 | 7.751 | 367.73 | 13.654 | 1765.69 |
| 4.159 | 47.10 | 7.971 | 403.44 | 13.734 | 1736.15 |
| 4.188 | 45.89 | 8.098 | 415.85 | 14.211 | 1986.10 |
| 4.482 | 63.58 | 8.391 | 470.64 | 14.359 | 2077.26 |
| 4.552 | 66.80 | 8.507 | 477.00 | 14.668 | 2123.23 |
| 4.728 | 70.22 | 8.872 | 554.53 | 14.868 | 2296.86 |
| 4.854 | 83.04 | 8.995 | 561.78 | 15.204 | 2316.53 |
| 5.003 | 90.80 | 9.281 | 626.78 | 15.453 | 2460.26 |
| 5.194 | 105.40 | 9.486 | 683.99 | 16.005 | 2642.64 |
| 5.221 | 105.38 | 9.619 | 692.78 | 16.176 | 2746.47 |
| 5.453 | 124.95 | 9.922 | 737.91 | 16.908 | 2986.11 |
| 5.461 | 124.44 | 9.967 | 774.53 | 16.948 | 3033.33 |
| 5.759 | 151.06 | 10.333 | 845.04 | 17.773 | 3334.06 |
| 5.764 | 147.79 | 10.348 | 832.07 | 17.811 | 3407.37 |
| 6.013 | 166.57 | 10.746 | 961.31 | 18.609 | 3723.14 |
| 6.042 | 168.48 | 10.835 | 961.69 | 18.762 | 3744.73 |
| 6.291 | 188.42 | 11.186 | 1061.41 | 19.419 | 4090.47 |
| 6.293 | 198.40 | 11.355 | 1071.69 | 19.629 | 4161.10 |
| 6.544 | 216.95 | 11.717 | 1210.82 | | |

Table A (4). Heat capacity of $La_5Pb_3$ II

| T (deg K) | C (mJ/g-at K) | T (deg K) | C (mJ/g-at K) |
|---|---|---|---|
| 2.575 | 12.05 | 5.096 | 98.35 |
| 2.597 | 12.81 | 5.155 | 104.84 |
| 2.606 | 12.31 | 5.177 | 109.99 |
| 2.682 | 14.44 | 5.226 | 110.06 |
| 3.188 | 20.01 | 5.332 | 118.28 |
| 3.217 | 24.80 | 5.363 | 118.98 |
| 3.243 | 20.37 | 5.383 | 121.75 |
| 3.289 | 27.16 | 5.419 | 122.33 |
| 3.626 | 32.52 | 5.557 | 136.69 |
| 3.670 | 32.16 | 5.574 | 136.57 |
| 3.727 | 34.76 | 5.610 | 140.69 |
| 3.780 | 37.65 | 5.680 | 142.42 |
| 3.922 | 37.91 | 5.777 | 155.18 |
| 3.990 | 46.37 | 5.808 | 155.07 |
| 4.057 | 49.12 | 5.833 | 160.64 |
| 4.071 | 46.45 | 5.961 | 167.07 |
| 4.171 | 46.90 | 6.009 | 174.80 |
| 4.265 | 58.28 | 6.040 | 177.19 |
| 4.292 | 58.31 | 6.063 | 179.45 |
| 4.383 | 54.48 | 6.194 | 189.30 |
| 4.403 | 56.58 | 6.254 | 197.48 |
| 4.485 | 68.29 | 6.274 | 198.09 |
| 4.512 | 70.59 | 6.316 | 206.46 |
| 4.608 | 66.79 | 6.408 | 211.86 |
| 4.662 | 72.80 | 6.525 | 224.99 |
| 4.679 | 78.66 | 6.655 | 237.78 |
| 4.766 | 84.78 | 6.782 | 250.73 |
| 4.826 | 82.80 | 6.916 | 268.61 |
| 4.878 | 92.93 | 7.057 | 288.32 |
| 4.920 | 85.05 | 7.197 | 302.70 |
| 4.964 | 96.28 | 7.331 | 317.11 |
| 5.047 | 99.04 | | |

Table A(5). Heat capacity of $La_5Pb_3C$

| T (deg K) | C (mJ/g-at K) | T (deg K) | C (mJ/g-at K) | T (deg K) | C (mJ/g-at K) |
|---|---|---|---|---|---|
| 2.588 | 10.39 | 6.162 | 113.02 | 10.942 | 822.50 |
| 2.634 | 9.33 | 6.192 | 118.28 | 11.251 | 909.49 |
| 2.797 | 11.85 | 6.344 | 129.63 | 11.435 | 939.58 |
| 3.089 | 13.76 | 6.487 | 138.61 | 11.538 | 982.78 |
| 3.136 | 15.18 | 6.513 | 145.06 | 11.881 | 1054.43 |
| 3.204 | 14.53 | 6.733 | 168.29 | 11.911 | 1087.45 |
| 3.289 | 15.99 | 6.828 | 173.52 | 12.338 | 1148.55 |
| 3.496 | 20.82 | 6.919 | 190.96 | 12.361 | 1157.27 |
| 3.607 | 20.54 | 7.125 | 208.13 | 12.786 | 1306.61 |
| 3.620 | 21.64 | 7.187 | 208.88 | 12.882 | 1320.33 |
| 3.831 | 23.61 | 7.363 | 235.85 | 13.221 | 1446.80 |
| 3.903 | 26.16 | 7.505 | 242.91 | 13.465 | 1516.35 |
| 3.948 | 26.70 | 7.627 | 261.86 | 13.756 | 1602.67 |
| 4.017 | 28.02 | 7.829 | 282.88 | 14.045 | 1719.91 |
| 4.136 | 32.62 | 7.891 | 296.26 | 14.393 | 1799.15 |
| 4.316 | 29.43 | 8.173 | 333.75 | 14.628 | 1905.02 |
| 4.353 | 32.50 | 8.214 | 330.05 | 15.058 | 2078.92 |
| 4.399 | 35.41 | 8.451 | 375.44 | 15.182 | 2093.30 |
| 4.414 | 38.02 | 8.617 | 390.94 | 15.679 | 2287.26 |
| 4.566 | 41.64 | 8.765 | 420.11 | 15.773 | 2314.91 |
| 4.635 | 45.59 | 9.013 | 457.65 | 16.379 | 2601.56 |
| 4.832 | 50.97 | 9.041 | 451.63 | 16.387 | 2579.44 |
| 4.885 | 51.63 | 9.305 | 512.72 | 17.045 | 2842.76 |
| 5.093 | 61.00 | 9.462 | 527.77 | 17.151 | 2933.75 |
| 5.236 | 63.56 | 9.646 | 560.04 | 17.746 | 3130.57 |
| 5.303 | 78.91 | 9.945 | 620.70 | 18.055 | 3269.21 |
| 5.507 | 80.92 | 9.977 | 634.67 | 18.401 | 3481.73 |
| 5.552 | 84.57 | 10.268 | 683.11 | 19.058 | 3816.79 |
| 5.686 | 86.90 | 10.430 | 711.01 | 19.087 | 3851.62 |
| 5.859 | 99.32 | 10.570 | 751.93 | 19.732 | 4208.15 |
| 5.886 | 100.73 | 10.927 | 837.05 | 20.025 | 4378.06 |
| 6.005 | 104.26 | | | | |