LOW TEMPERATURE SPECIFIC HEAT OF SOME RARE EARTH-ALUMINUM LAVES PHASE COMPOUNDS

by

Richard Edwin Hungsberg

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Signatures have been redacted for privacy

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INTRODUCTION

This investigation was part of a larger study of the physical properties of rare earth Laves phase compounds. These materials are characterized by the AB_2 stoichiometry in which the A atom is always the larger. In the cubic $MgCu_2$ (C15) type structure, the B atoms lie on the corners of tetrahedra which are arranged point to point in the crystal leaving holes for the A atoms.

Assuming a rigid sphere model for the cubic phase, there are only A-A and B-B contacts between atoms if the ratio of the radius of the A atom to the radius of the B atom is 1.225 (the ideal packing ratio). A radius ratio greater than the ideal value results in only A atoms in contact. Only B-B contacts exist when the ratio is less than 1.225. For hard spheres there are never any A-B contacts.

AB_2 compounds are known to form from atoms with radius ratios, r_A/r_B, ranging from less than 1.1 to greater than 1.5. When combining, the constituent atoms probably adjust their sizes to bring r_A/r_B nearer to the ideal radius ratio. In general the A atom is more compressible, and several authors (1,2,3) have suggested that a more meaningful radius ratio can be calculated by assuming that only the A atom changes in size. Its radius in the compound can be calculated from a knowledge of the geometry of the Laves phase; $r_A^{calc} = \underline{a}\sqrt{3}/8$, where $\underline{a}$ is the lattice parameter. A new radius ratio, r_A^{calc}/r_B, (where r_B is the radius of the B atom determined from its elemental structure) can then be used to predict what type of contacts are present in the compound.

A correlation has been observed (1) between the Laves phase radius ratios and Debye temperatures, θ, obtained from low temperature specific heat and elastic constant measurements. It was found that when r_A^{calc}/r_B was greater than 1.225, the θ for that compound was closer to the θ for pure A than to the θ for pure B. Similarly when r_A^{calc}/r_B was less than the ideal value, θ for the Laves phase was closer to the Debye temperature of the B component.

The Debye temperature, a parameter describing the thermal behavior of materials, is frequently encountered in solid state physics (4). θ is proportional to the maximum frequency of atomic vibration in a solid and is related to the rigidity of an atomic lattice, a high θ indicating a rigid lattice with strong interatomic force constants. Specific heat measurements are one of a number of methods from which Debye θ values may be obtained.

At liquid helium temperatures the specific heat of a normal metal is found to obey the following relation

$$C = \beta T^3 + \gamma T \qquad (1)$$

where γT is the electronic contribution to the specific heat and βT^3 is the lattice contribution. From an analysis of the lattice vibrations, it has been shown (4) that when $T \ll \theta$, the Debye temperature can be obtained from the expression for the lattice contribution

$$\beta T^3 = 12\pi^4 R T^3 / 5\theta^3 \qquad (2)$$

where R is the gas constant and T is the temperature in Kelvin degrees.

From the free-electron theory of metals the electronic specific heat is found to be

$$\gamma T = \pi^2 k^2 V N(\epsilon_F) T/3 \qquad (3)$$

where k is Boltzmann's constant, V the molar volume, and $N(\epsilon_F)$ the density of states at the Fermi level. When T is low enough for Equation 1 to be obeyed, a plot of C/T versus T^2 will be linear. β and thus θ can be obtained from the slope, and γ will be the T = 0K intercept.

One of the objects of this investigation is to measure the low temperature specific heat of the RAl_2 (R = Y, La, Lu) Laves phases in order to determine their γ and θ values.

These values should help to increase our understanding of the nature of Laves phase compounds. Furthermore, another objective is to determine if the Debye temperatures obtained will correlate with calculated radius ratios.

SAMPLE PREPARATION

The impurity contents of the materials used in this investigation are given in Table 1.

All three compounds were prepared by arc melting weighed amounts of the components on a water cooled copper hearth under a zirconium gettered argon atmosphere. To obtain homogeneity, each sample was turned over and remelted one or more times. Shattering or cracking of the brittle samples occurred upon restriking of the arc. This was prevented by turning them over immediately on the hearth and restriking the arc while still red hot. To prevent cracking, power to the arc was reduced as much as possible after the last melting to allow the sample to cool down as slowly as possible.

Metallographic examination and x-ray analysis indicated that the $LaAl_2$ and YAl_2 samples were single phase and homogeneous (Figures 1 and 2 respectively). Keller's solution (1 ml HF, 1½ ml HCl, 2½ ml HNO_3, 95 ml H_2O) was used to etch the RAl_2 compounds. The $LuAl_2$ was found to have a small amount of a second phase. Point count analysis revealed the two phase area to be 8 to 16% of the total area (Figure 3). Higher power magnification showed the second phase occupying 25% of the two phase area (Figure 4). Thus, about 2 to 4%

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

	Starting materials			
Impurity	Al	Y	La	Lu
H	-	5	29	6
C	-	-	36	10
N	-	12	78	9
O	-	175	79	107
F	-	-	19	<3
Mg	10	-	≤10	-
Al	M	-	≤10	-
Si	10	-	≤10	-
Ca	-	-	≤10	-
Sc	-	-	-	1
Cr	-	-	≤10	0.3
Mn	<10	-	-	-
Fe	10	-	≤40	2.4
Ni	-	-	100	2
Cu	20	-	20	10
Zn	<10	-	-	-
Y	-	M	-	2.5
La	-	-	M	16
Ce	-	-	≤350	2
Pr	-	-	≤150	12
Nd	-	-	≤100	4
Gd	-	-	-	2
Tb	-	-	-	3
Dy	-	-	-	2
Ho	-	-	-	9
Er	-	-	-	3
Ta	-	-	≤500	100

< less than

≤ less than or equal to

\- not analyzed for

M major component

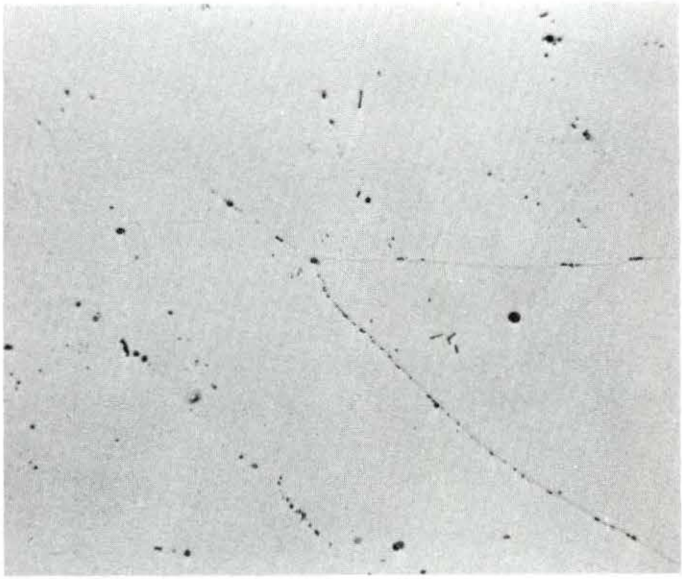

Figure 1. Photomicrograph of $LaAl_2$, 250X

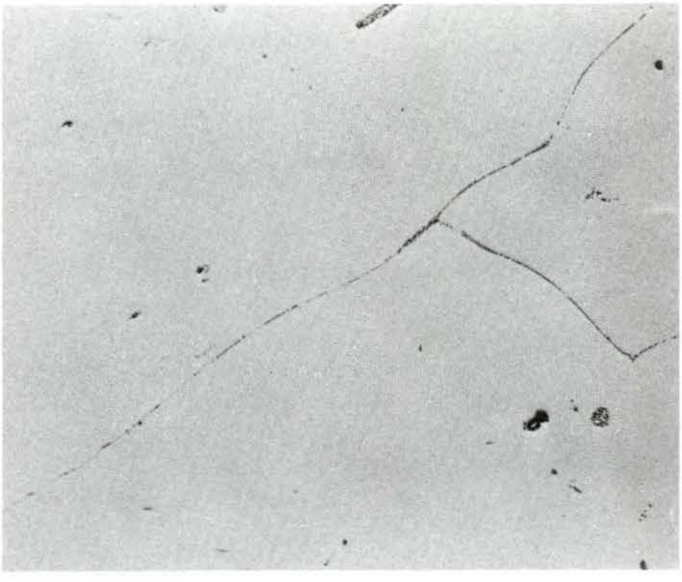

Figure 2. Photomicrograph of YAl_2, 250X

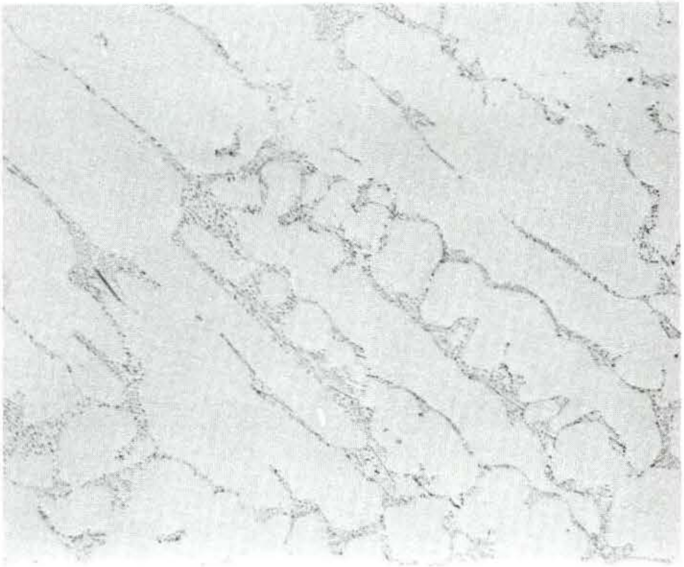

Figure 3. Photomicrograph of $LuAl_2$, 250X

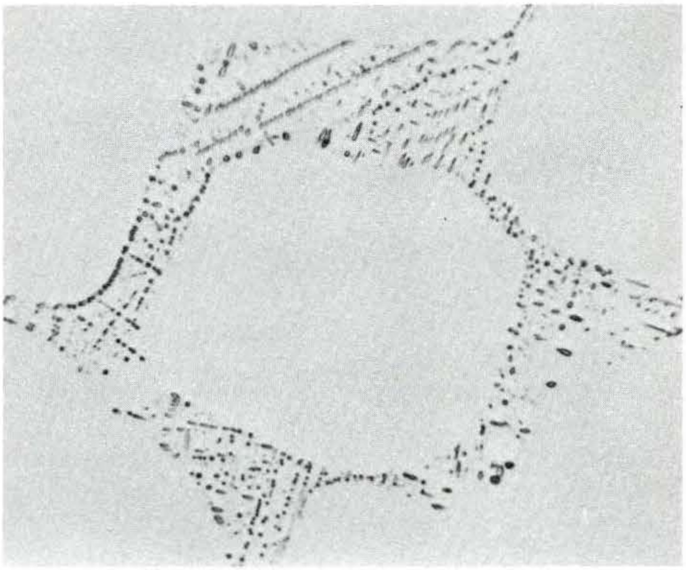

Figure 4. Photomicrograph of $LuAl_2$, 1000X

of the second phase was present, and any affect on the specific heat data should be small (this point is discussed later).

A conventional spark cutter was used to cut two parallel faces on the samples to allow mounting in the calorimeter. Because the compounds were very brittle, small portions broke off even with careful handling. Sample surfaces left unprotected for several weeks remained bright and shiny, indicating very little or no oxidation.

The lattice parameter for the $LaAl_2$ prepared was 8.148 ± 0.001Å. This agrees well with the reported constants of 8.153 ± 0.005Å (5) and 8.145 ± 0.005Å (6,7). YAl_2 was found to have a = 7.864 ± 0.001Å and compares with a reported value of 7.857 Å (8). X-ray analysis of $LuAl_2$ yielded a = 7.743 ± 0.001Å, which compares to a reported value of 7.742Å (9).

CALORIMETRY

Specific heat measurements were made in an adiabatic calorimeter built by Dr. R. R. Joseph (10) and modified by N. T. Panousis (11). Since the details of the apparatus have already been described by Dr. Joseph, only a brief account of the operating procedure will be given here. A sample is placed in the calorimeter which is then evacuated. After cooling the apparatus and sample in a liquid helium dewar, the sample is thermally isolated. A heat pulse is given to the sample using a calibrated electrical heater for a measured period of time. The temperature of the sample is monitored with a calibrated germanium resistance thermometer. Knowing the heat input and temperature rise, the heat capacity of the sample can be calculated.

The accuracy of the calorimetry was checked by measuring the specific heat of a Calorimetry Conference Copper Standard (12). Measured values agreed with published copper data (12, 13) to within one percent in the temperature range of 2.5 to 20 K.

RESULTS

Experimental values of specific heat and temperature for each of the Laves phases are given in the appendix. Figure 5 is a plot of C/T versus T^2 for YAl_2 over the entire temperature range covered. The linear portion of the data is shown expanded in Figure 6. Fitting of the points to the equation $C/T = \gamma + \beta T^2$ yielded $\gamma = 5.47$ mj/mole-K^2, $\beta = 0.0538$ mj/mole-K^4, and $\theta = 331$ K.

The $LuAl_2$ data (Figures 7 and 8) were handled in a similar manner, giving for γ, β, and θ 5.60 mj/mole-K^2, 0.106 mj/mole-K^4, and 264 K respectively. γ and θ may be in error due to the presence of a second phase in this sample. It was possible to calculate errors in the observed gamma, γ_{obs}, assuming that it was a linear combination of the γ values for the $LuAl_2$ and second phase. An error of less than 3% would result from a second phase gamma, γ_2, between 0.5 and 11.0 mj/mole-K^2. If γ_2 were unusually high such as 25.mj/mole-K^2, γ_{obs} could be in error by as much as 10%. A similar analysis indicated a maximum error of 2% in the observed θ for second phase thetas in the range of 100 to 400 K.

C/T versus T^2 data for $LaAl_2$, shown in Figures 9 and 10, yielded $\beta = 0.125$ mj/mole-K^4, $\theta = 249$ K, and $\gamma = 11.0$

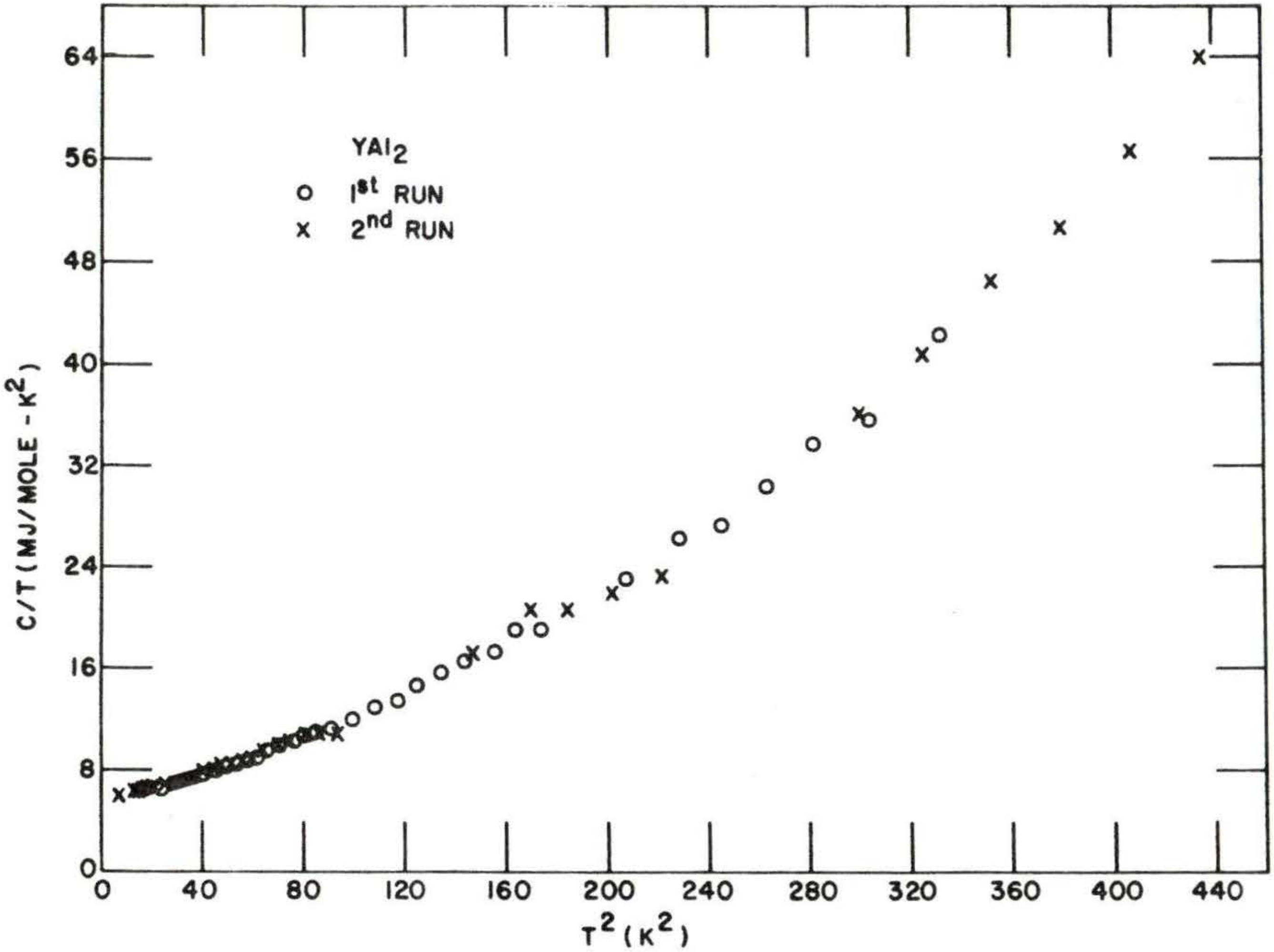

Figure 5. Specific heat of YAl$_2$

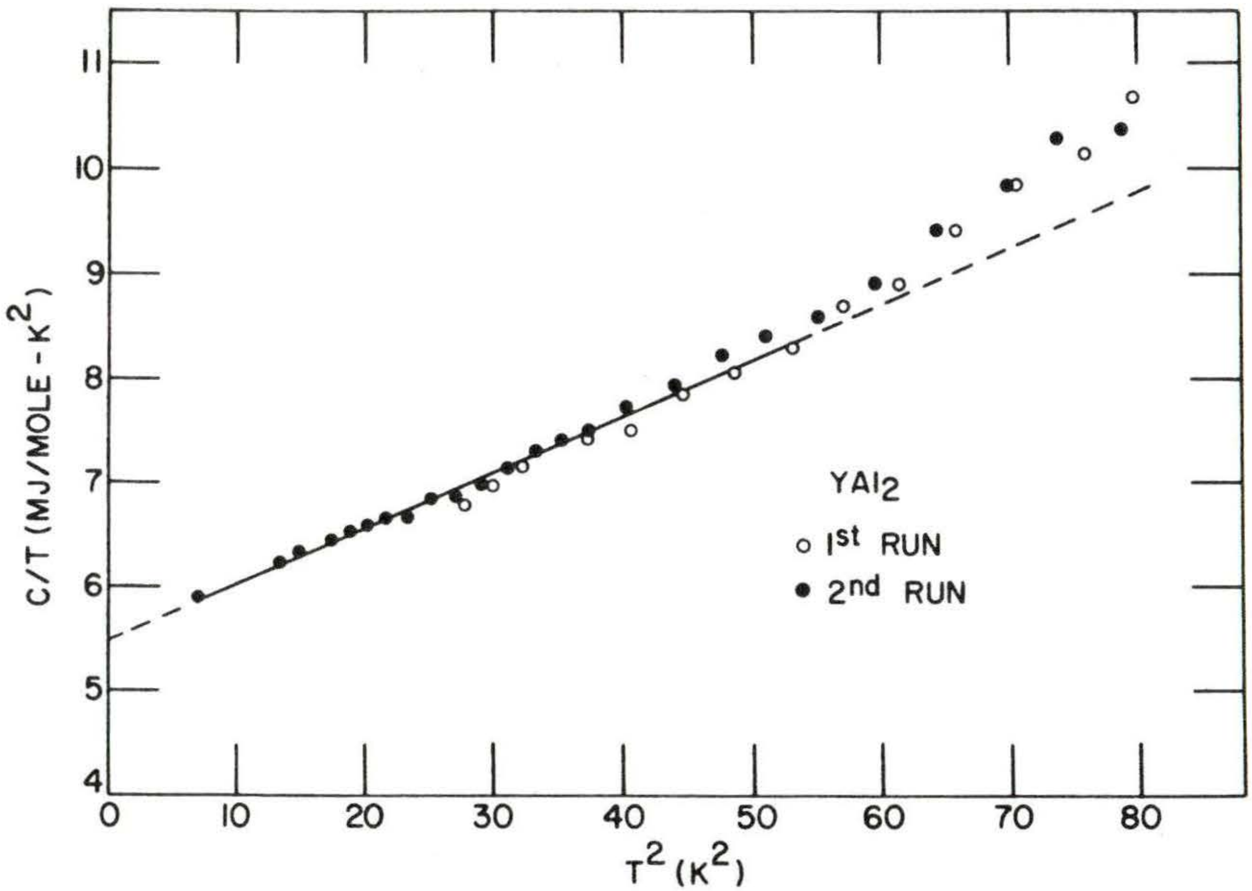

Figure 6. Specific heat of YAl$_2$

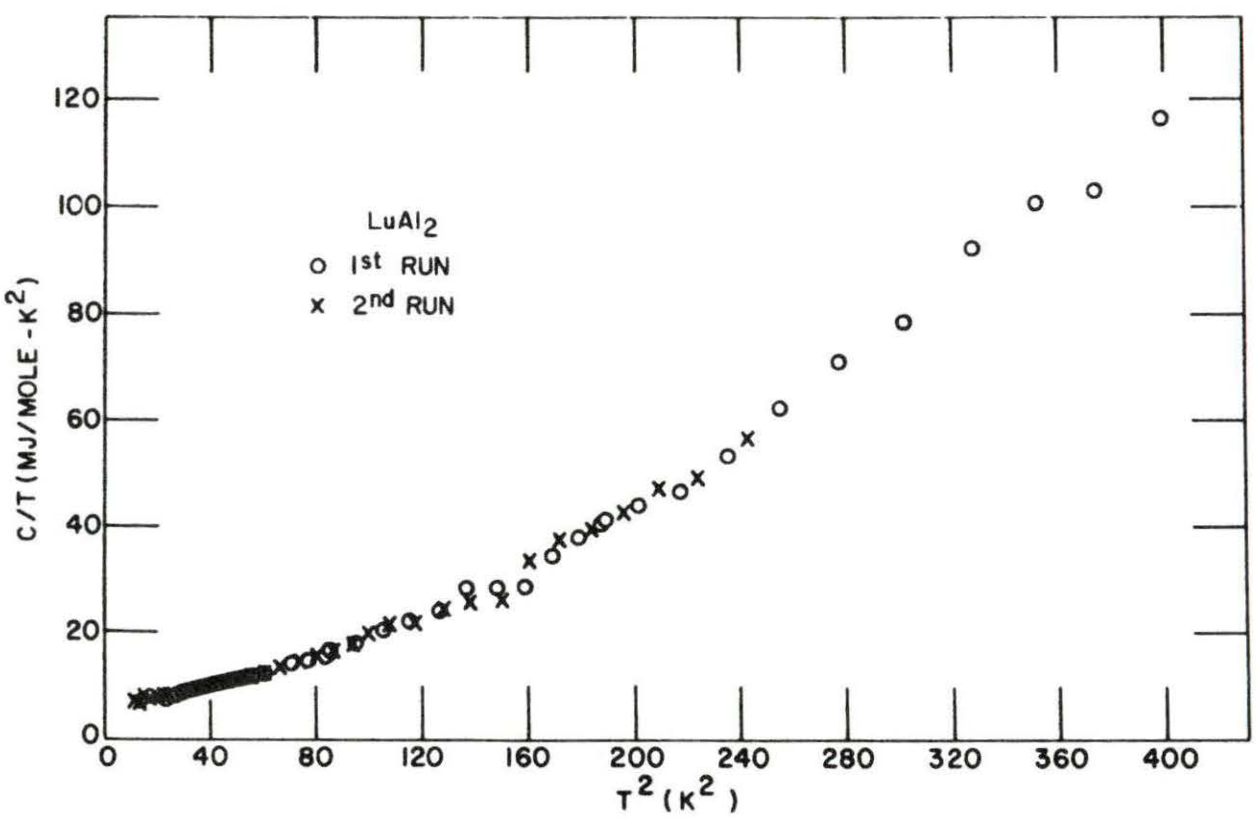

Figure 7. Specific heat of $LuAl_2$

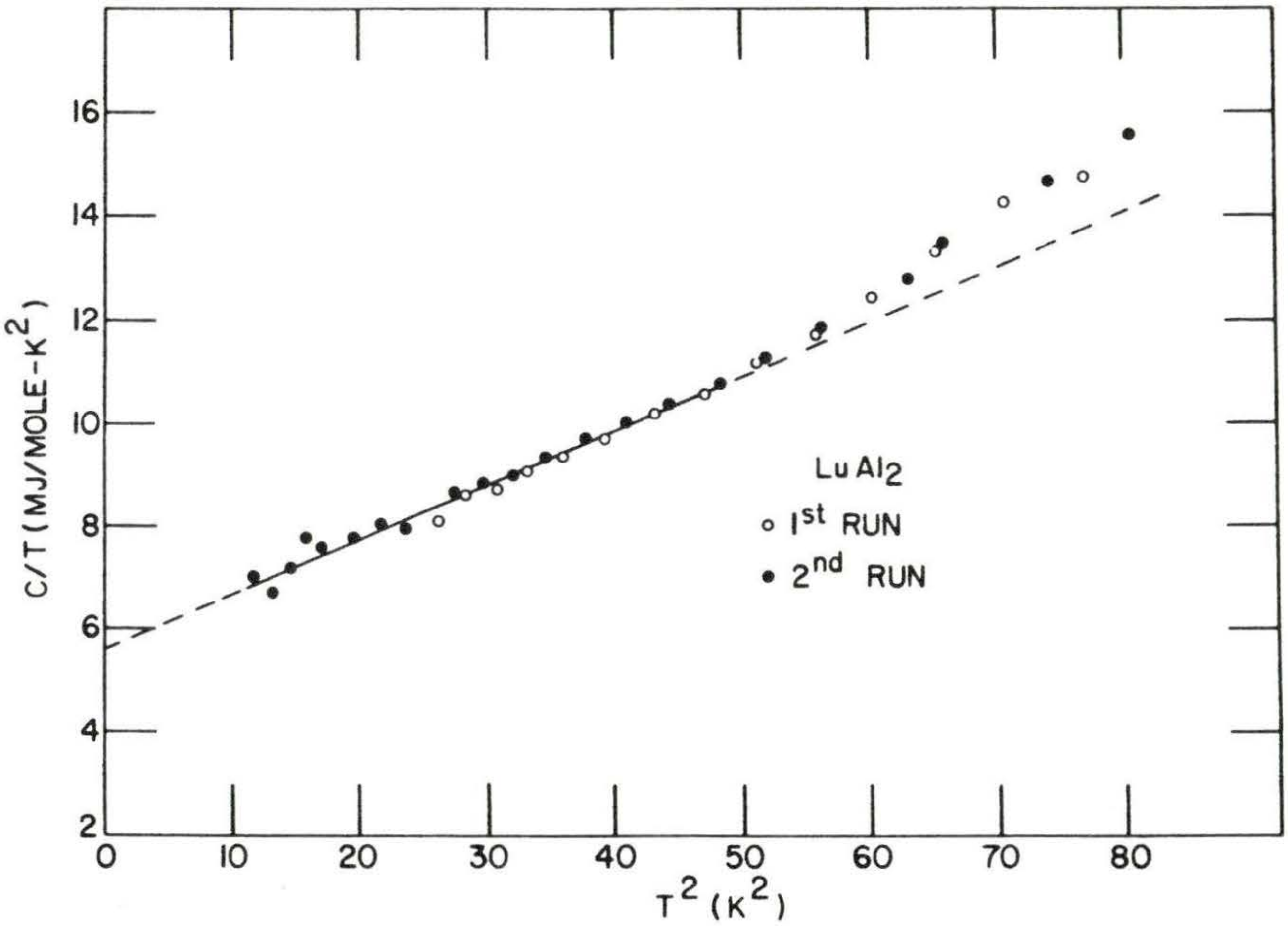

Figure 8. Specific heat of LuAl$_2$

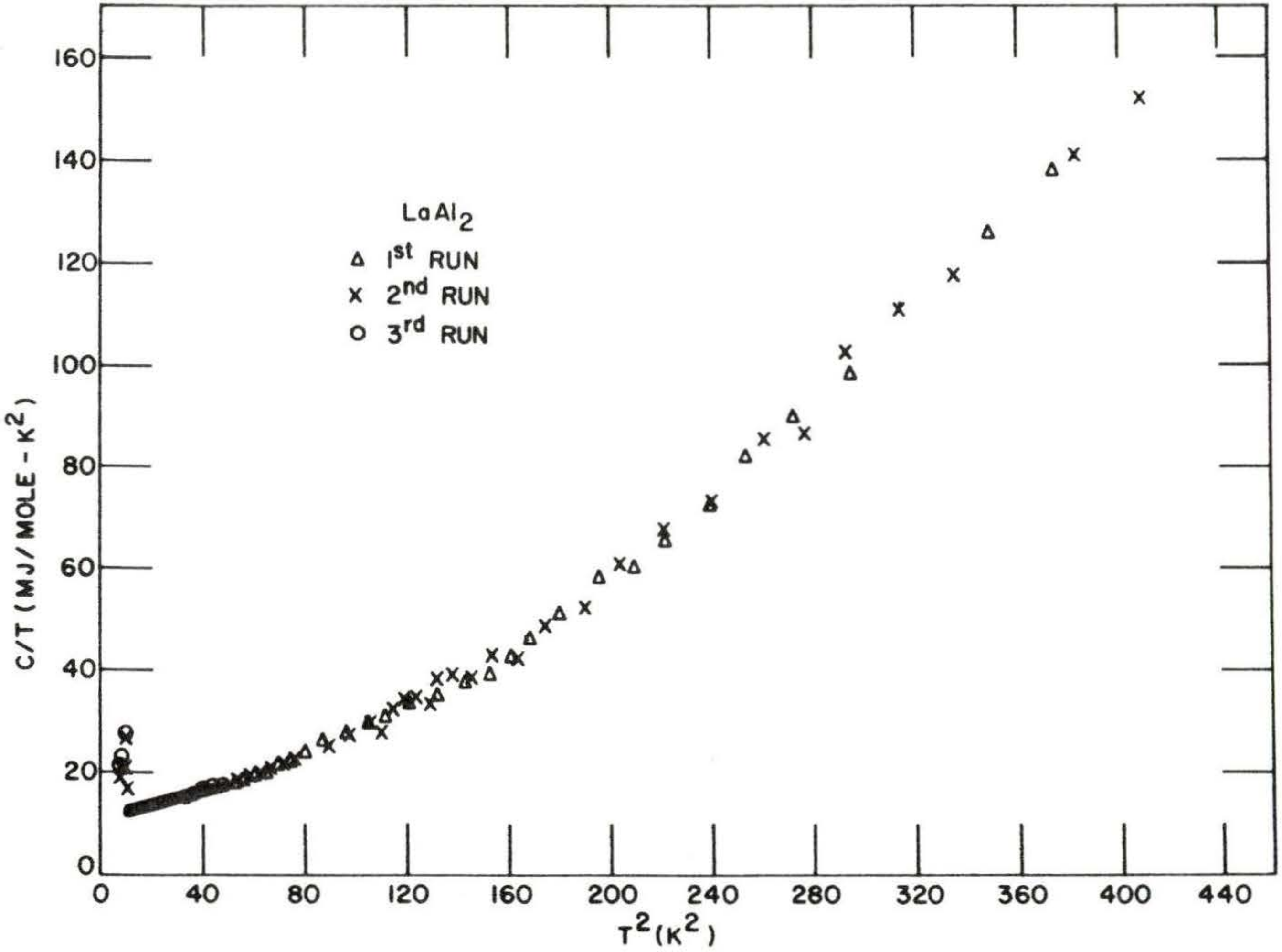

Figure 9. Specific heat of $LaAl_2$

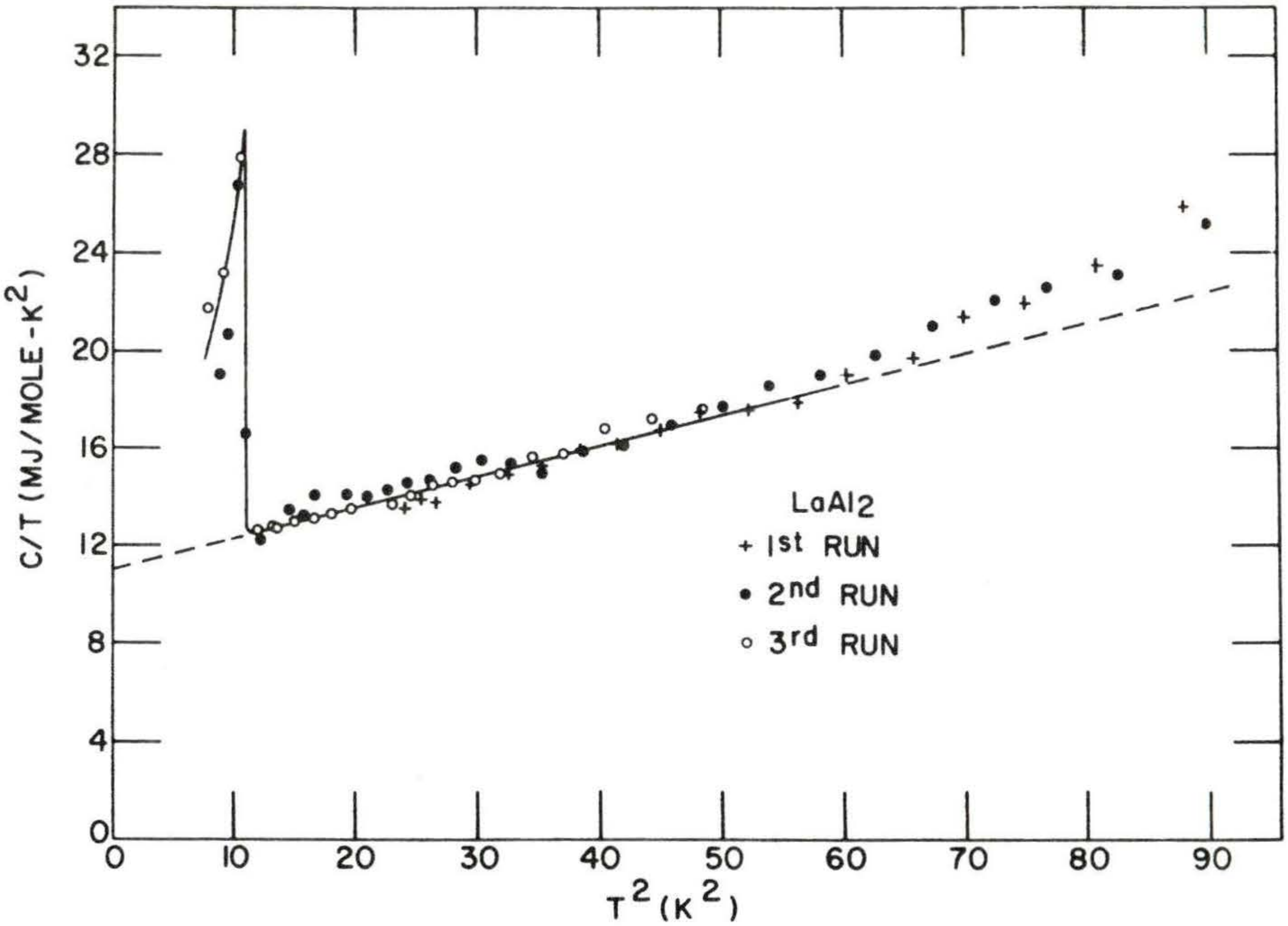

Figure 10. Specific heat of $LaAl_2$

mj/mole-K^2. The peak at 3.29 ± 0.03 K has a shape typical of a superconducting transition and is in good agreement with a reported (14,15) superconducting transition temperature of 3.2 K obtained from resistivity measurements. Other specific heat data (16) on $LaAl_2$ in the temperature range of 10 to 280 K agree with present values in the overlapping range of 14 to 20 Kelvin.

DISCUSSION

An extension of a treatment by Kittel (17) predicts that for a polyatomic lattice, the Debye temperature is inversely proportional to the square root of the mass of the atoms per formula unit. The results for the three RAl_2 compounds were examined to determine if that relationship was followed. Debye thetas, θ_{RAl_2}, relative to YAl_2 were calculated from the equation

$$\frac{(M_{YAl_2})^{\frac{1}{2}}}{(M_{RAl_2})^{\frac{1}{2}}} = \frac{\theta_{RAl_2}}{\theta_{YAl_2}} \qquad (4)$$

where M_{RAl_2} is the mass of the atoms per formula unit of RAl_2.

Table 2. Comparison of Debye temperatures and formula masses

Compound	$(M_{RAl_2})^{\frac{1}{2}}$	Calculated θ	Observed θ
YAl_2	11.95	331	331
$LaAl_2$	13.89	285	249
$LuAl_2$	15.13	262	264

Table 2 shows that the computed θ for $LaAl_2$ is larger than the θ observed. The close agreement of the calculated and observed Debye thetas for YAl_2 and $LuAl_2$ show them to be consistent with the relationship expressed in Equation 4.

A comparison of the Laves phase Debye thetas with those of the pure metals is shown in Table 3.

Table 3. Comparison of Debye temperatures

Compound	r_A/r_B	r_A^{calc}/r_B	θ_A(18)	θ_B(18)	θ_{RAl_2}
$LaAl_2$	1.311	1.232	142	423	249
YAl_2	1.238	1.188	268	423	331
$LuAl_2$	1.211	1.170	210	423	264

It can be seen from Table 3 that for each of the compounds the θ_{RAl_2} is closer to θ_A implying that near absolute zero lattice dynamics are controlled more by A-A contacts than by B-B contacts. This does not agree with the YAl_2 and $LuAl_2$ contacts predicted by r_A^{calc}/r_B. For YAl_2 this could be because of rare earth atoms not contracting as much as assumed in the r_A^{calc} computation. The Debye temperature for $LaAl_2$ fits the correlation since its radius ratio is greater than the ideal packing ratio.

The γ value for the La compound (approximately twice those for YAl_2 and $LuAl_2$) may account for the fact that $LaAl_2$ was the only one of the three found to be superconducting. Its corresponding higher density of states at the Fermi level is consistent with recent theories (19,20) which associate a high density of states with superconductivity. Gamma values (see Table 4) from other Laves phase specific heat data were examined, and most were found to follow the same pattern. Those compounds with γ less than 10 mj/mole-K^2 were not observed to become superconducting. The Laves phases with higher γ values did (with one exception) have a superconducting transition.

Table 4. Comparison of Laves phase γ values

Compound	γ(mj/mole-K^2)	T_s(K)	Reference
YAl_2	5.47	-	-
$LaAl_2$	11.0	3.29	-
$LuAl_2$	5.60	-	-
$LaPt_2$	1.17	-	(10)
$CePt_2$	~1.17	-	(10)
$LaRu_2$	13.6	3.20	(10)
$CeRu_2$	23.3	5.92	(10)
$CeRu_{1.9}Pt_{0.1}$	10.3	4.08	(21)
$CeRu_{1.8}Pt_{0.2}$	11.1	3.40	(21)
$CeNi_2$	10.3	-	(22)
$MgCu_2$	3.117	-	(23)

T_s = superconducting transition temperature

The present γ values for the RAl_2 compounds are reasonable when compared with existing data for other Laves phases.

SUMMARY

Specific heats, C, of three rare earth Laves phase compounds YAl_2, $LaAl_2$, and $LuAl_2$ were measured in the temperature range of 2.5 to 20 K. A superconducting transition was observed in $LaAl_2$ at 3.29 Kelvin. C/T versus T^2 data yielded $\gamma_{YAl_2} = 5.47$ mj/mole-K^2, $\gamma_{LaAl_2} = 11.0$ mj/mole-K^2, $\gamma_{LuAl_2} = 5.60$ mj/mole-K^2, $\theta_{YAl_2} = 331$ K, $\theta_{LaAl_2} = 249$ K, and $\theta_{LuAl_2} = 264$ K.

Debye thetas for YAl_2 and $LuAl_2$ implied that A-A contacts dominate at low temperatures, not B-B contacts as predicted by their radius ratios. θ_{LaAl_2} and $r_{La}{}^{calc}/r_{Al}$ both indicated A-A atom contacts, and thus the $LaAl_2$ data agreed with the radius ratio and Debye temperature correlation.

Gamma values for the RAl_2 compounds and other Laves phases were compared. A correlation between the gammas and the existence of superconductivity was observed. Those compounds with γ less than 10 mj/mole-K^2 did not become superconducting. The Laves phases with higher γ values did (with one exception) have a superconducting transition.

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APPENDIX

Measured Specific Heats

MEASURED SPECIFIC HEAT OF LA-AL2

T (DEG K)	C (MJ/MOLE-K)	T (DEG K)	C (MJ/MOLE-K)	T (DEG K)	C (MJ/MOLE-K)
2.816	61.52	5.949	89.21	10.779	349.49
2.960	56.21	5.948	91.04	10.958	376.95
3.030	70.23	6.091	96.26	11.055	371.21
3.078	63.85	6.190	98.64	11.179	386.07
3.208	86.10	6.213	98.52	11.416	380.41
3.236	90.36	6.359	107.03	11.526	403.28
3.322	55.25	6.444	104.23	11.544	441.71
3.471	43.81	6.483	104.47	11.796	462.19
3.509	42.78	6.657	114.47	11.986	447.33
3.663	46.85	6.704	112.28	12.110	470.03
3.687	47.05	6.778	114.90	12.389	481.97
3.826	51.72	6.938	121.31	12.436	532.15
3.887	50.41	6.958	122.64	12.696	536.21
3.957	52.47	7.087	125.73	12.834	544.94
4.078	53.47	7.223	127.04	13.017	598.33
4.082	57.65	7.348	136.64	13.261	643.96
4.256	56.85	7.499	134.32	13.447	681.04
4.389	62.04	7.631	144.94	13.837	724.41
4.436	60.06	7.775	148.08	14.008	808.73
4.583	64.39	7.920	156.87	14.318	870.49
4.768	68.31	8.111	159.81	14.509	868.12
4.790	65.54	8.208	172.10	14.922	1009.81
4.911	66.59	8.360	178.76	14.937	973.56
4.933	71.95	8.523	188.14	15.494	1116.76
4.964	69.53	8.663	190.20	15.538	1138.11
5.049	69.97	8.771	198.70	15.953	1303.54
5.124	75.28	8.994	211.49	16.182	1383.47
5.135	74.41	9.094	210.14	16.531	1483.51
5.162	71.08	9.389	243.18	16.657	1441.45
5.292	77.21	9.488	239.20	17.157	1756.69
5.321	80.86	9.835	270.96	17.195	1686.78
5.422	78.81	9.912	273.64	17.746	1962.95
5.464	80.23	10.269	300.61	18.339	2153.08
5.521	85.53	10.328	306.89	18.695	2346.93
5.648	84.34	10.539	293.01	19.367	2666.75
5.709	85.31	10.625	329.09	19.589	2756.24
5.731	88.41	10.646	329.27	20.244	3072.39
5.875	91.63				

MEASURED SPECIFIC HEAT OF Y-AL2

T (DEG K)	C (MJ/MOLE-K)	T (DEG K)	C (MJ/MOLE-K)	T (DEG K)	C (MJ/MOLE-K)
2.643	15.59	6.982	56.31	11.583	180.25
3.668	22.81	7.148	60.01	11.989	196.55
3.856	24.39	7.294	60.36	12.120	207.17
4.179	26.94	7.427	63.84	12.460	214.58
4.337	28.30	7.555	65.67	12.777	241.39
4.490	29.53	7.711	68.65	13.030	267.06
4.660	31.01	7.835	69.71	13.180	249.89
4.836	32.23	8.022	75.61	13.580	279.71
5.020	34.37	8.110	76.17	14.195	310.42
5.209	35.80	8.368	82.25	14.393	330.94
5.265	35.69	8.401	82.76	14.892	343.80
5.396	37.68	8.593	88.30	15.108	395.14
5.474	38.14	8.719	88.46	15.663	424.60
5.586	39.89	8.884	92.15	16.213	489.89
5.680	40.59	8.930	95.34	16.786	563.69
5.775	42.27	9.194	100.66	17.315	623.87
5.937	43.93	9.257	100.07	17.441	619.98
6.109	45.35	9.538	106.79	18.034	734.16
6.116	45.94	9.649	104.39	18.214	770.02
6.350	49.11	9.957	118.34	18.780	870.91
6.381	47.87	10.389	133.54	19.490	985.84
6.639	52.72	10.831	144.48	20.202	1142.34
6.675	52.39	11.160	162.66	20.868	1330.43
6.907	56.86				

MEASURED SPECIFIC HEAT OF LU-AL2

T (DEG K)	C (MJ/MOLE-K)	T (DEG K)	C (MJ/MOLE-K)	T (DEG K)	C (MJ/MOLE-K)
3.416	23.91	7.206	81.28	12.184	345.99
3.629	24.24	7.474	87.49	12.256	319.02
3.831	27.53	7.499	88.91	12.596	359.44
3.988	31.00	7.766	96.34	12.673	422.62
4.135	31.37	7.808	99.81	13.007	448.36
4.426	34.36	8.079	107.79	13.115	491.40
4.670	37.41	8.120	109.39	13.389	510.11
4.868	38.51	8.411	119.94	13.563	535.64
5.122	41.46	8.610	126.17	13.701	553.58
5.231	45.30	8.771	129.19	13.752	564.99
5.331	45.66	8.971	139.12	14.011	595.49
5.445	47.98	9.228	154.72	14.194	622.05
5.549	48.35	9.316	157.14	14.480	680.20
5.669	51.04	9.697	171.95	14.753	686.65
5.774	52.36	9.748	173.86	14.975	733.97
5.891	55.00	9.997	197.27	15.355	815.98
6.005	56.17	10.250	209.05	15.589	883.31
6.147	59.75	10.388	224.27	15.985	993.68
6.270	60.84	10.738	237.83	16.663	1180.86
6.399	64.27	10.839	234.71	17.391	1363.39
6.572	66.83	11.238	269.56	18.113	1669.22
6.666	69.28	11.307	277.64	18.773	1890.24
6.860	72.31	11.695	330.98	19.361	1994.13
6.948	74.74	11.761	301.42	20.005	2326.77
7.153	79.99				