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Low Temperature Heat Capacities and Related Thermal Properties of $TbAl_2$ and $HoAl_2$*

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Heat capacities of $TbAl_2$ and $HoAl_2$ for the range 5 to 300 K are presented. The magnetic contribution, (C_p)mag, for $TbAl_2$ is very broad, resembling that for $GdAl_2$. (C_p)mag for $HoAl_2$ is generally similar but, in addition, peaks in C_p are observed at 20 and 28 K. The measured magnetic entropies for the two compounds are only about 80% of $R\ln(2J+1)$. The possibility cannot be excluded that the ground state is doubly degenerate in these cases. The data are treated to give values of the Third Law Entropy (S), $H - H_0°$ and $F - H_0°$.

Introduction

This study is part of a continuing series of investigations dealing with the heat capacities of rare earth intermetallics. The present study is an extension of earlier work on several of the $LnAl_2$ compounds (*1*). Most of the $LnAl_2$ compounds (Ln is a lanthanide) become ferromagnetic at low temperatures. The destruction of ferromagnetism gives, of course, a contribution to the heat capacity. Studies of the heat capacity behavior are being undertaken in part to determine the dependence of the magnetic heat capacity on temperature.

In the preceding study measurements were made on $LnAl_2$ with Ln = La, Ce, Pr, Nd and Gd. The influence of magnetic ordering was clearly evident in the results for the Pr, Nd and Gd compounds. $PrAl_2$ and $NdAl_2$ exhibited sharp λ-type thermal anomalies. The magnetic heat capacity for $GdAl_2$ was not λ-type but instead was spread over a wide range of temperatures. Since $GdAl_2$ was the only compound in the series previously studied containing a heavy rare earth [$4f$ (*7–14*)], it was not clear whether its peculiar behavior was unique to Gd, characteristic of heavy rare earths or perhaps of heavy lanthanides with odd numbers of f electrons. The present work was undertaken partly to clarify this point and partly to provide thermodynamic data for additional $LnAl_2$ compounds.

Experimental Methods

Samples were prepared using the best grade metals available commercially—99.9% pure (exclusive of possible gaseous impurities) rare earths and 99.999% pure Al. The metals were fused together by induction heating in a water-cooled copper boat under argon, the so-called cold boat method. Since these compounds form congruently, only a brief strain annealling procedure (1 hr at 1000°C) was deemed necessary. The samples were analyzed by X-ray diffraction and metallographic techniques to ascertain that they were single phase materials. The diffraction results confirmed them to exist in the $MgCu_2$ structure. Masses used in the calorimeter were 58.4610 g for $TbAl_2$ and 73.9370 for $HoAl_2$.

The calorimetric technique has been described in an earlier publication from this laboratory (*2*).

Results and Discussion

Experimental results[1] are largely summarized in Figs. 1 and 2. T_c obtained from magnetic measurements (*3*) is also indicated on the diagrams. Clearly, the excess heat capacity

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[1] Tables giving the raw heat capacity data have been deposited as Document No. NAPS-02134 with ASIS National Auxiliary Publication Service, c/o CCM Information Co., 909 Third Ave., New York, NY 10022. A copy may be secured by citing the document number and by remitting $5.00 for photocopies or $1.50 for microfiche.

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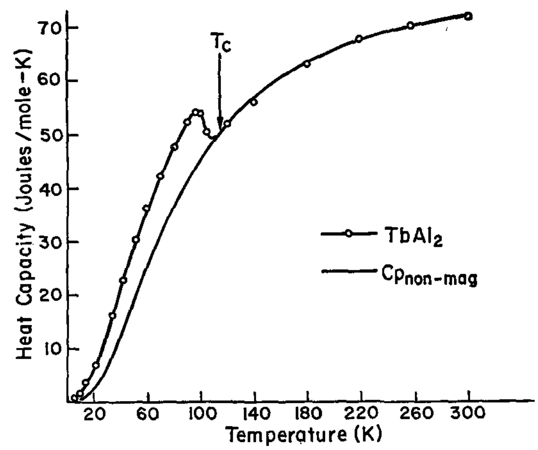

FIG. 1. Heat capacities of $TbAl_2$ and C_p(nonmag) vs temperature. For details as to how C_p(nonmag) is evaluated, see text.

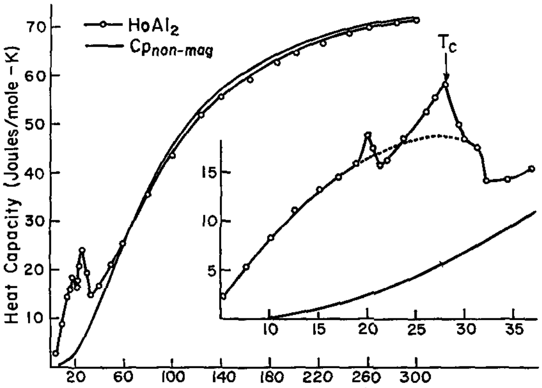

FIG. 2. Heat capacities of $HoAl_2$ and C_p(nonmag) vs temperature.

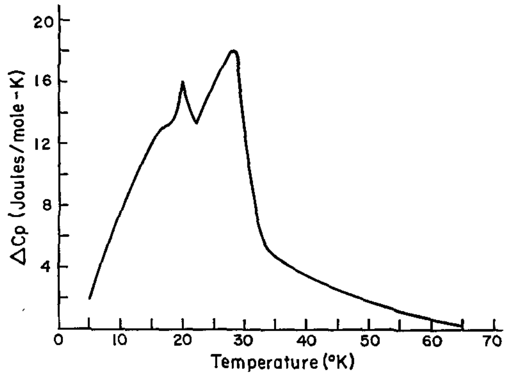

FIG. 4. Magnetic heat capacity of $HoAl_2$ vs temperature.

associated with the destruction of ferromagnetism in $TbAl_2$ *is not* λ-type but is instead broad, being significant at all temperatures studied. Thus results for $TbAl_2$, an even $4f$ electron system, closely resemble those for $GdAl_2$, an odd $4f$ electron system. This excludes the possibility that the broad magnetic thermal anomaly is an odd $4f$ electron effect.

Results for $HoAl_2$ upon superficial examination seem rather different from those obtained for $GdAl_2$ and $TbAl_2$ but upon more careful scrutiny they seem rather similar. The C_p data for $HoAl_2$ show pronounced peaks at about 20 and 28 K which are superimposed on a broad thermal anomaly similar to that exhibited by $TbAl_2$. The prominence of the peaks in C_p versus T plot tends to obscure the fact that the magnetic entropy associated with the peaks (i.e., that part which corresponds to the excess over the broken

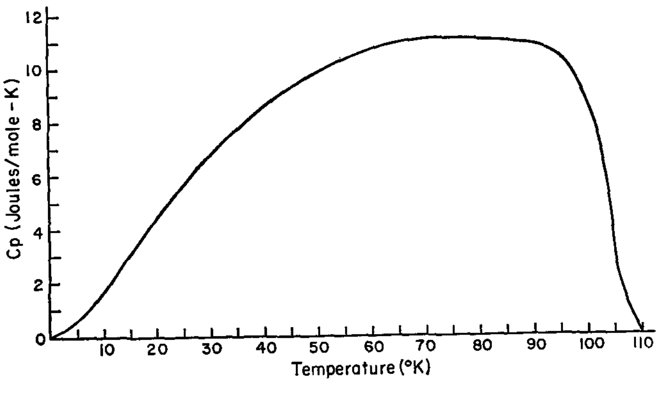

FIG. 3. Magnetic heat capacity of $TbAl_2$ vs temperature.

TABLE I

MAGNETIC ENTROPIES OF $TbAl_2$ AND $HoAl_2$

	$R\ln(2J+1)$(J/mole K)	ΔS(exp)(J/mole K)
$TbAl_2$	21.3	17.4
$HoAl_2$	23.5	20.2

TABLE II

SMOOTHED HEAT CAPACITIES AND THERMODYNAMIC VALUES FOR $TbAl_2$

Temp. (K)	Heat capacity (J/mole K)	Entropy (J/mole K)	$(H-H_0°)$ (J/mole)	$-(F-H_0°)$ (J/mole)
5.00	0.22	0.14	0.40	0.30
10.00	1.69	0.65	4.50	2.03
15.00	3.94	1.75	18.35	7.84
20.00	6.80	3.26	44.97	20.18
25.00	10.03	5.12	86.93	40.99
30.00	13.66	7.27	146.15	71.84
35.00	17.41	9.65	223.79	114.05
40.00	21.23	12.23	320.40	168.68
45.00	25.03	14.95	436.07	236.56
50.00	28.74	17.78	570.53	318.33
55.00	32.31	20.69	723.21	414.46
60.00	35.72	23.64	893.35	525.27
70.00	41.97	29.63	1282.39	791.59
80.00	47.46	38.60	1932.95	1155.29
90.00	51.97	44.46	2430.90	1570.75
100.00	53.95	50.10	2966.55	2043.88
110.00	48.91	54.93	3471.81	2569.94
120.00	51.39	59.29	8973.73	3141.15
130.00	53.81	63.50	4499.73	3755.22
140.00	56.07	67.57	5048.94	4410.67
150.00	58.16	71.51	5620.27	5106.17
160.00	60.02	75.32	6211.33	5840.44
170.00	61.67	79.01	6819.94	6612.22
180.00	63.13	82.58	7444.09	7420.29
190.00	64.41	86.03	8081.92	8263.42
200.00	65.54	89.36	8731.79	9140.46
210.00	66.53	92.58	9392.23	10,050.28
220.00	67.39	95.70	10,061.92	10,991.78
230.00	68.16	98.71	10,739.76	11,963.91
240.00	68.84	101.63	11,424.80	12,965.68
250.00	69.45	104.45	12,116.29	13,996.14
260.00	70.01	107.19	12,813.64	15,054.38
270.00	70.55	109.84	13,516.45	16,135.56
280.00	71.07	112.41	14,224.51	17,250.87
290.00	71.59	114.92	14,937.77	18,387.56
300.00	72.14	117.35	15,656.37	19,548.94
273.15	70.71	110.66	13,738.93	16,486.84
298.15	72.03	116.91	15,523.01	19,332.26

TABLE III

SMOOTHED HEAT CAPACITIES AND THERMODYNAMIC VALUES FOR $HoAl_2$

Temp. (K)	Heat capacity (J/mole K)	Entropy (J/mole K)	Enthalpy (J/mole)	$-(F-H_0°)$ (J/mole)
10.00	7.84	6.21	33.40	28.68
15.00	13.03	10.49	87.12	70.25
19.50	16.40	14.27	152.23	126.04
20.00	18.10	14.70	160.76	133.29
20.50	17.48	15.16	169.99	140.75
25.00	20.00	18.51	246.31	216.41
28.00	23.72	20.99	312.13	275.63
30.00	18.84	22.47	354.90	319.18
34.00	13.70	24.45	417.94	413.41
46.00	18.89	29.30	612.02	735.82
50.00	20.86	30.96	691.51	856.33
55.00	23.36	33.06	802.06	1016.36
60.00	25.90	35.20	925.03	1187.00
65.00	28.42	37.37	1060.89	1368.42
70.00	30.84	39.57	1209.12	1560.77
80.00	35.37	43.99	1540.58	1978.55
90.00	39.50	48.40	1915.30	2440.51
100.00	43.24	52.76	2329.38	7946.33
110.00	46.63	57.04	2779.10	3495.39
120.00	49.68	61.23	3260.96	4086.83
130.00	52.41	65.32	3771.68	4719.65
140.00	54.84	69.29	4308.20	5392.81
150.00	57.01	73.15	4867.73	6105.14
160.00	58.94	76.90	5447.72	6885.49
170.00	60.65	80.52	6045.86	7642.68
180.00	62.16	84.03	6660.07	8465.56
190.00	63.50	87.43	7288.53	9322.96
200.00	64.69	97.72	7929.65	10,213.8
210.00	65.76	93.90	8582.02	11,137.0
220.00	66.72	96.98	9244.50	12,091.5
230.00	67.58	99.97	9916.09	13,076.3
240.00	68.38	102.86	10,596.0	14,090.5
250.00	69.11	105.67	11,283.5	15,133.2
260.00	69.79	108.39	11,978.0	16,203.6
270.00	70.43	111.04	12,679.2	17,300.8
280.00	71.03	113.61	13,386.6	18,424.1
290.00	71.60	116.11	14,099.8	19,572.7
300.00	72.13	118.55	14,818.5	20,746.1
273.15	70.62	111.86	12,901.3	17,651.9
298.15	72.03	118.11	14,685.1	20,527.2

line in Fig. 2) is only 3% of the total magnetic entropy of the system.

In regard to the magnetic contribution to entropy and heat capacity it is clear that the measured heat capacity includes lattice and electronic contribution. Consequently an estimate of these contributions must be made to extract the magnetic heat capacity from the total. This is accomplished ordinarily by using a nonmagnetic analog of the magnetic compound. $LaAl_2$ and $LuAl_2$ would be appropriate in this respect but data are available only for $LaAl_2$ (*1*). Comparing results obtained for $TbAl_2$, $HoAl_2$ and $LaAl_2$ it was found that at temperatures above T_c C_p for the lanthanum compound exceeds C_p for $TbAl_2$ and $HoAl_2$, the excess amounting to 1–2% at 300 K. This indicates that results for $LaAl_2$ do not constitute a satisfactory representation of the nonmagnetic heat capacity contributions for $TbAl_2$ and $HoAl_2$. The studies of Hungsberg and Gschneidner (*4*) suggested that the large heat capacity of $LaAl_2$ originates with the electronic term. They found γ, the electronic specific heat coefficient, for $LaAl_2$ to be 11.0 mJ/K^2 mole, which is almost double the value for $LuAl_2$, 5.7. The enlarged γ value for $LaAl_2$ is ascribed to the enhanced density of states resulting from the proximity of the $4f$ levels to the Fermi energy in $LaAl_2$. With increasing atomic number the f states decrease in energy to a point well below the Fermi limit; under these circumstances the enhancement due to f-level proximity disappears and γ decreases. It thus appears that γ for $TbAl_2$ or $HoAl_2$ should be closer to the value for $LuAl_2$ than that for $LaAl_2$. Accordingly a better approximation of the nonmagnetic (nm) contribution to the heat capacity C_{nm}, is obtained from the expression

$$(C_p)_{nm} = (C_p)_{\mathrm{LaAl2}} - (\Delta\gamma)T,$$

where $\Delta\gamma = \gamma_{\mathrm{LaAl_2}} - \gamma_{\mathrm{LuAl_2}}$. $(C_p)_{nm}$ is plotted in Figs. 1 and 2.

$(C_p)\mathrm{mag} = C_p - (C_p)_{nm}$. This is plotted for $TbAl_2$ and $HoAl_2$ in Figs. 3 and 4. Experimental magnetic entropies together with the theoretica-value, $R\ln(2J+1)$ are listed in Table 1. Experimental values shown in Table I are 15 to 20% lower than the theoretical values in keeping with experience in this laboratory with other rare earth intermetallics (*1*, *2*, *5*, *6*). The cause of the discrepancy is as yet not clear. It may be due to inadequacies in estimating C_{nm}. Alternatively, it may be a consequence of two low lying crystal field states by coincidence having nearly the same energy so that the system behaves as if the ground state is a doublet. Detailed analysis of $ErNi_5$ (*7*) shows that this situation can occur.

Smoothed heat capacities and the usual derived thermodynamic properties are given in Tables II and III. These data were obtained from the raw data by standard calculational procedures. Extrapolation of C_p to 0 K was accomplished with the use of unpublished data (*8*) for the temperature range 1.5 to 10 K.

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