

## Low Temperature Heat Capacity and Magnetic Studies on $\text{DyCu}_5$

K. S. V. L. NARASIMHAN, M. J. KLEIN AND R. A. BUTERA

*Department of Chemistry, University of Pittsburgh, Pittsburgh,  
Pennsylvania 15260*

Received September 11, 1974

Low temperature heat capacity studies on  $\text{DyCu}_5$  revealed a  $\lambda$ -anomaly at 6.55 K. Evaluation of the entropy indicated that the ground state is not  $(2J + 1)$  fold degenerate. High field magnetization data yield a moment of  $9.28 \mu_B$  at 4.2 K and 120 kOe.

### Introduction

$\text{RCu}_5$  compounds ( $R = \text{Tb}$  to  $\text{Tm}$ ) crystallize in the cubic  $\text{AuBe}_5$  type of structure (1). The magnetic properties of these materials indicate a change from antiferro to ferromagnetic ordering as we progress from Tb to Ho (2). Since the magnetic interactions in these compounds are generally attributed to the indirect exchange interaction of the *RKKY* type it is surprising a change in the magnetic ordering takes place without any change in the electron concentration. Another interesting feature is that the extrapolated saturation moments observed at low temperatures are considerably lower than the  $gJ$  value (2). These measurements were carried out in fields of 30 kOe and hence the observed moments are not indicative of saturation value. Even if saturation is reached the presence of crystal field effects from the rare earth could alter the moment. We investigated the low temperature heat capacity (1.4 to 11 K) and high field magnetization (120 kOe) on  $\text{DyCu}_5$  in order to ascertain the nature of magnetic ordering.

### Experimental

The samples were prepared by induction melting the dysprosium (99.9% pure) and copper (99.999% pure) in a water cooled copper boat under a flowing atmosphere of purified argon gas. The compound was cast

into an ingot form and hemispherical buttons by using a proper shape of the cold boat. The button and the ingot were wrapped in a tantalum foil and annealed for three weeks at 800°C.

The purity of the compounds was checked by X-ray diffraction on annealed powders. These studies were carried out using a Philips diffractometer equipped with a Debye-Scherrer Camera and  $\text{CuK}\alpha$  radiation. All the lines in the diffraction pattern could be indexed as belonging to the  $\text{AuBe}_5$  type of structure. The lattice constant was obtained from the powder photographs utilizing a least-squares computer program and is shown in Table I.

Heat capacity measurements were carried out on buttons (~5 gm) using an isothermal pulse calorimeter. The details of the measurement are described elsewhere (3). Magnetic measurements were carried out using a Faraday technique from 4.2 K to room temperature in fields up to 20 kOe. High field measurements at 4.2 K were carried out using a 120 kOe superconducting magnet in conjunction with a moving sample magnetometer. The precision in the measurement of magnetization is better than 0.1%; the accuracy is estimated to be 1%.

### Results and Discussion

Magnetization vs temperature data are shown in Fig. 1. The maximum in the magnetization suggests antiferromagnetic ordering

TABLE I  
MAGNETIC AND HEAT CAPACITY DATA FOR  $\text{DyCu}_5$

Néel temperature (from $C_p$ data)	Néel temperature (from Mag. data at two applied fields)		Saturation moment $\mu_B/\text{F.U.}$	Paramagnetic effective moment $\mu_B/\text{F.U.}$	Weiss temperature	Lattice constant $a$
6.55 K	6 kOe 7 K	20 kOe 3 K	4.2 K, 120 kOe 9.28	10.7	-1 K	$7.026 \pm 0.002$

at 7 K in an applied field of 6 kOe and at 3 K in an applied field of 20 kOe. Buschow et al. (2) also measured the magnetization of  $\text{DyCu}_5$  and they attribute the absence of a Néel temperature in applied field of 30 kOe down to 2.1 K as due to metamagnetism of the material. Magnetization vs field data are shown in Fig. 2. The magnetization increases linearly up to an applied field of 9 kOe and with further increase of field a transition takes place and saturation is reached at 120 kOe. This behavior is typical of an antiferromagnet with a low exchange field. Using a molecular field approximation (5) we calculated an exchange field of 52 kOe for  $\text{DyCu}_5$ . This value of exchange field is overcome easily by the applied field and saturation is attained. The magnetic moment at 120 kOe is  $9.28 \mu_B$ , which

is lower than the  $gJ$  value for  $\text{Dy}^{+3}$  ion ( $10 \mu_B$ ). In the paramagnetic region a Curie-Weiss behavior was observed with effective moment shown in Table I.

Results of the heat capacity measurements are shown in Table II and Fig. 2. The  $\lambda$ -anomaly associated with the antiferromagnetic ordering is observed at 6.55 K. A closer look at the  $\lambda$ -anomaly reveals that it is opposite to that observed for a normal antiferromagnet. For  $T > T_N$  there is a slow decrease in the heat capacity, whereas for  $T < T_N$  there is a sharp decrease in the heat capacity. The entropy under this peak could be estimated if the lattice and electronic contribution to the heat capacity were known. Unfortunately  $\text{LaCu}_5$  does not crystallize in the  $\text{AuBe}_5$  type of structure and  $\text{LuCu}_5$  is not reported to exist.  $\text{UCu}_5$  was thought to be a good blank but magnetic data indicate an antiferromagnetic type of ordering at 15 K (6). An estimate of the entropy without correcting for the lattice and electronic contribution from a plot of  $C_p/T$  vs  $T$  for  $\text{DyCu}_5$  would give a rough idea of the energy level distribution. Such an estimation yields a value of 12.96 joules/mole, which is

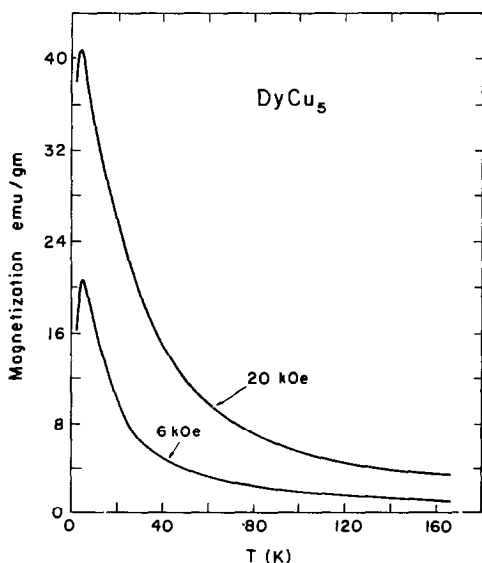


FIG. 1. Magnetization vs temperature at 6 kOe and 20 kOe for  $\text{DyCu}_5$ .

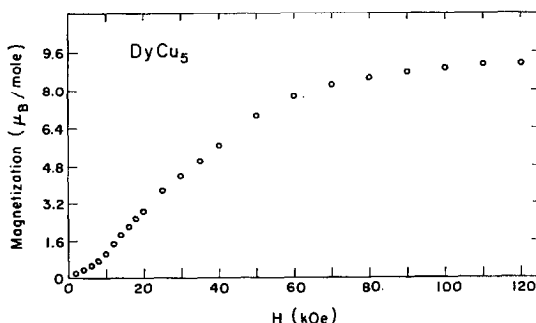


FIG. 2. Magnetization vs field at 4.2 K for  $\text{DyCu}_5$ .

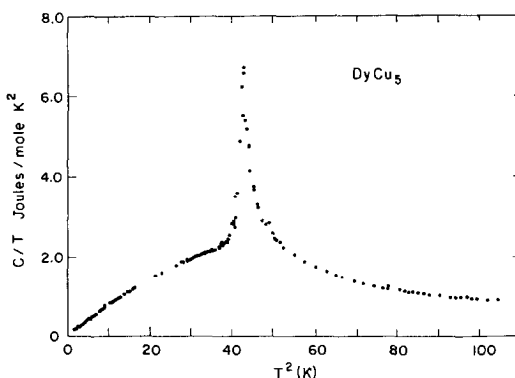
TABLE II

MOLAR HEAT CAPACITY DATA FOR DyCu<sub>5</sub>

T (K)	C <sub>p</sub> joules/ mole-deg K	T (K)	C <sub>p</sub> joules/ mole-deg K
1.44	0.236	5.82	12.292
1.51	0.267	5.88	12.490
1.64	0.330	5.94	12.839
1.75	0.405	6.00	13.160
1.87	0.498	6.06	13.573
2.00	0.609	6.12	13.802
2.12	0.729	6.18	14.451
2.23	0.857	6.24	15.166
2.35	1.004	6.35	18.155
2.57	1.323	6.40	22.902
2.69	1.502	6.51	36.121
2.81	1.720	6.53	43.108
2.94	1.960	6.56	35.501
3.06	2.211	6.60	31.356
3.19	2.486	6.65	27.592
3.31	2.780	6.69	25.225
3.44	3.084	6.10	14.551
3.57	3.428	6.15	14.429
3.76	4.060	6.21	14.670
3.87	4.299	6.27	15.795
4.08	4.949	6.33	17.826
4.28	5.622	6.39	22.306
4.49	6.369	6.44	31.440
4.89	8.048	6.48	40.517
5.10	8.956	6.51	43.785
5.33	10.001	6.57	34.199
5.77	12.169	6.61	31.675
5.99	13.259	6.66	27.693
6.38	22.148	6.71	24.694
6.65	27.927	6.76	22.436
7.16	17.017	6.87	19.957
7.39	15.413	6.98	19.738
7.66	13.975	7.04	18.324
7.93	12.815	7.11	17.314
8.23	11.884	7.18	16.913
8.46	7.599	8.35	11.589
4.79	7.599	8.48	11.268
5.14	9.180	8.62	11.018
5.26	9.793	8.76	10.707
5.40	10.422	9.03	10.380
5.53	11.077	9.16	10.174
5.66	11.717	9.30	10.063
5.79	12.352	9.70	9.675
5.93	13.003	9.84	9.653
6.07	13.758	9.97	9.579
6.20	14.760	10.10	9.466
6.33	17.816	10.23	9.328
6.37	18.833	10.36	9.171

TABLE II (continued)

5.31	9.866	8.82	10.757
5.41	10.290	8.96	10.411
5.47	10.604	9.10	10.135
5.53	10.883	9.23	10.020
5.59	11.262	9.37	9.989
5.65	11.524	9.51	9.789
5.71	11.761	9.65	9.596
5.77	11.970	9.78	9.623
5.84	12.371	9.90	9.470
5.91	12.686	6.68	20.866
5.98	13.083	6.78	21.812
6.05	13.475	6.93	19.426
6.12	13.959	7.09	17.489
6.20	14.593	7.24	16.178
5.63	11.396	7.40	15.249
5.70	11.677	8.15	12.209
5.76	11.971	8.83	11.301

FIG. 3.  $C_p/T$  vs  $T^2$  plot for DyCu<sub>5</sub>.

much smaller than  $R \ln(2J+1)$  expected for Dy<sup>3+</sup>. This suggests that the ground state is fourfold degenerate and strong crystalline field effects are present. Magnetic measurements on the other hand reveal a moment of  $9.28 \mu_B$  ( $gJ$  for Dy<sup>3+</sup> =  $10 \mu_B$ ). From the heat capacity and magnetic data we could conclude that the ground state includes a  $15/2$  state and is fourfold degenerate.

Heat capacity measurements at higher temperatures extending up to 300 K are essential in understanding the details of the crystal field splittings in the DyCu<sub>5</sub>. This would also help in making a detailed point charge calculation to describe the heat capacity behavior from 1.4 to 300 K.

**Acknowledgments**

We are thankful to Dr. W. E. Wallace and Dr. R. S. Craig for their interest in this work and Dr. D. A. Keller for several fruitful discussions.

**References**

1. K. H. J. BUSCHOW, A. S. VAN DER GOOT, AND J. BIRKHAM, *J. Less Common Metals* **19**, 433 (1969)
2. K. H. J. BUSCHOW, A. M. VANDIEPEN, AND DE WIJN, *J. Appl. Phys.* **41**, 4609 (1970).
3. K. S. V. L. NARASIMHAN, R. A. BUTERA, R. S. CRAIG, AND W. E. WALLACE, *J. Solid State Chem.* **9**, 267 (1974).
4. R. A. BUTERA (unpublished).
5. J. S. SMART, "Effective Field Theories of Magnetism," W. B. Saunders Company, Philadelphia, 1966.
6. K. S. V. L. NARASIMHAN (unpublished).