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Heat Capacities and Related Thermal Properties of $DyNi_5$, $HoNi_5$ and $ErNi_5$ Between 5 and 300 K*

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Heat capacity data and calculated thermodynamic functions are presented for $DyNi_5$, $HoNi_5$ and $ErNi_5$. λ-type thermal anomalies are noted at 12.0 K ($DyNi_5$), 4.1 K ($HoNi_5$) and 8.0 K ($ErNi_5$). Schottky-type anomalies are observed at higher temperatures. The λ and Schottky anomalies are ascribed to the destruction of ferromagnetic order and to crystal field excitation, respectively. A deficiency of magnetic entropy, compared to $R\ln(2J+1)$, is noted corresponding roughly to $R\ln 2$. This suggests that the ground state in the ordered materials is a doublet. $ErNi_5$ is analyzed using a Hamiltonian containing terms representing the crystal field and magnetic interactions. The analysis shows that a doublet ground state can result with reasonable values of the crystal field parameters. The parameters are shown to be consistent with the heat capacity behavior of $ErNi_5$. Ordering temperatures are not proportional to the de Gennes function.

Introduction

Low-temperature calorimetric studies of $LnNi_5$ compounds with Ln = La, Ce, Pr, Nd and Gd have recently been made in this laboratory (*1*, *2*). The loss of magnetic entropy of the lanthanide ion as the material is cooled toward absolute zero is observed to lead to a variety of thermal anomalies. With the single exception of $GdNi_5$ the previous studies have been concerned with compounds containing light lanthanides. It has seemed of interest to extend the measurements to include other heavy lanthanides. In this communication we report measurements made on $DyNi_5$, $HoNi_5$ and $ErNi_5$. These data have been used to extract the magnetic entropy and to compute values for the various thermodynamic functions.

Experimental Details

The method used in preparing the samples and most of the particulars of the calorimetric procedure have been described earlier (*1*, *3*). The only change over the earlier technique is the incorporation of an automatic data acquisition system (ADAS) into the procedure (*4*, *5*). With the ADAS results emerge in the form of punched cards, which can be used directly with the computer, eliminating errors that may enter when the data are processed manually.

Samples were prepared using the best grade lanthanide metals commercially obtainable (99.9% with respect to metallic impurities) and Johnson–Matthey spectroscopic nickel. The sample size for the measurements were as follows: 74.35 g for $DyNi_5$, 77.86 g for $HoNi_5$ and 73.77 g for $ErNi_5$.

Results and Discussion

The heat capacity results and the thermodynamic functions evaluated therefrom are displayed in Figs. 1 to 3 and Tables I to VI.[1] In

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[1] Tables I, II, and III giving the raw heat capacity data have been deposited as Document No. NAPS-02177 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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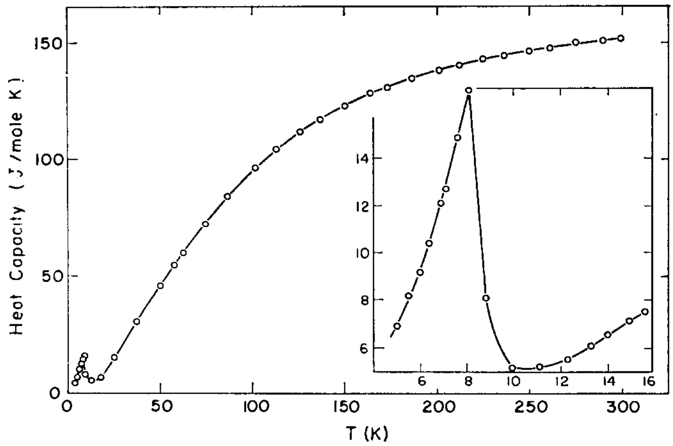

FIG. 1. Heat capacity of $DyNi_5$ vs temperature.

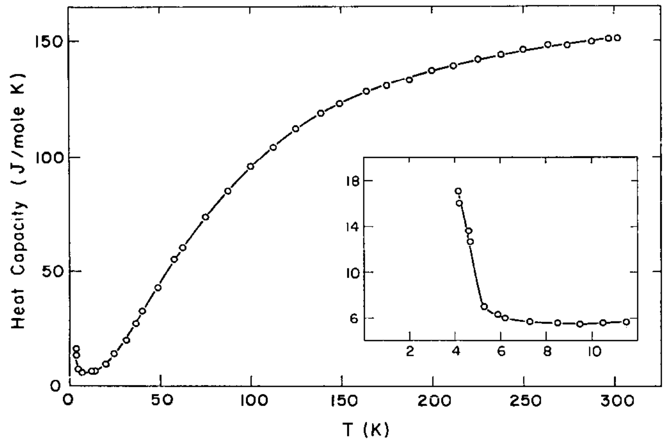

FIG. 2. Heat capacity of $HoNi_5$ vs temperature.

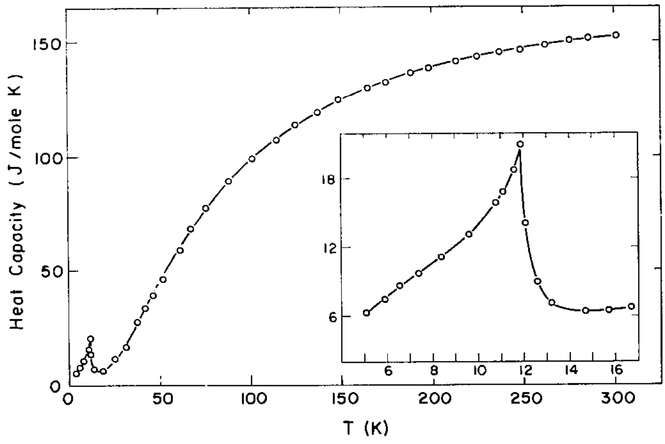

FIG. 3. Heat capacity of $ErNi_5$ vs temperature.

TABLE IV

SMOOTHED MOLAR HEAT CAPACITIES AND THERMODYNAMIC FUNCTIONS FOR $DyNi_5$[a]

T(K)	C_p (J/mole K)	S (J/mole K)	$\left(\frac{H-H_0^0}{T}\right)$ (J/mole K)	$-\left(\frac{G-H_0^0}{T}\right)$ (J/mole K)
4.0	3.28	1.29	0.91	0.39
5.0	5.00	2.21	1.55	0.66
6.0	6.78	3.28	2.28	1.00
7.0	8.54	4.46	3.05	1.41
8.0	10.20	5.71	3.84	1.87
9.0	12.33	7.03	4.66	2.37
10.0	14.10	8.42	5.51	2.90
11.0	16.80	9.88	6.41	3.47
12.0	21.35	11.51	7.44	4.07
15.0	6.12	13.35	7.56	5.78
20.0	8.40	15.37	7.45	7.93
25.0	12.68	17.68	8.04	9.64
50.0	44.80	35.78	18.01	17.77
75.0	75.00	59.83	32.12	27.71
100.0	97.60	84.70	45.84	38.86
125.0	113.89	108.37	57.94	50.43
150.0	125.07	130.18	68.25	61.93
175.0	132.98	150.09	76.97	73.12
200.0	138.82	168.24	84.35	83.89
225.0	143.43	184.87	90.67	94.20
250.0	147.29	200.19	96.14	104.05
273.15	150.26	213.36	100.61	112.76
298.15	152.56	226.63	104.87	121.76
300.0	152.68	227.57	105.17	122.41

[a] Data from Ref. (*6*) were utilized to calculate the thermodynamic functions below 10 K. Results in this Table and in Tables V and VI justify only four significant figures. The larger number of figures reported was provided by the computer; they are given to facilitate interpolations which are sometimes needed in calculations.

TABLE V

SMOOTHED MOLAR HEAT CAPACITIES AND THERMODYNAMIC FUNCTIONS FOR $HoNi_5$

T(K)	C_p (J/mole K)	S (J/mole K)	$\left(\frac{H-H_0^0}{T}\right)$ (J/mole K)	$-\left(\frac{G-H_0^0}{T}\right)$ (J/mole K)
4.0	9.60	4.25	3.01	1.25
4.4	11.60	5.26	3.70	1.56
4.8	14.12	6.37	4.45	1.92
5.0	10.00	6.88	4.78	2.11
6.0	6.18	8.18	5.15	3.02
10.0	5.46	11.07	5.35	5.72
15.0	6.80	13.47	5.55	7.92
20.0	9.93	15.81	6.22	9.60
25.0	14.50	18.50	7.40	11.10
50.0	45.18	37.60	18.36	19.24
75.0	74.04	61.61	32.30	29.31
100.0	96.14	86.09	45.64	40.46
125.0	111.83	109.31	57.37	51.93
150.0	123.25	130.77	67.46	63.31
175.0	131.28	150.40	76.03	74.37
200.0	137.45	168.35	83.34	85.01
225.0	142.56	184.84	89.64	95.20
250.0	146.43	200.08	95.14	104.94
273.15	148.77	213.15	99.59	113.56
298.15	151.61	226.29	103.82	122.47
300.0	151.97	227.23	104.12	123.11

calculating thermodynamic functions, use has been made of heat capacity data acquired using a pulse calorimeter over the range 1.5 to 10 K (*6*). Results obtained are in good agreement with the observed magnetic characteristics of these alloys (*7–9*). Typical λ-type anomalies are exhibited at temperatures between 4 and 12 K. These are attributed to the onset of ferromagnetic ordering. The Curie temperatures obtained from magnetic and heat capacity studies for $DyNi_5$, $HoNi_5$ and $ErNi_5$ together with other members of the series are presented in Table VII. The differences in the Curie temperatures in the two sets of measurements are attributable to the influence of the applied magnetic field in magnetization studies;

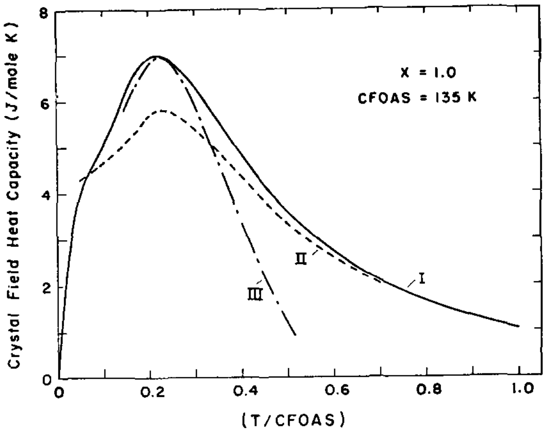

FIG. 4. Crystal field heat capacity of $ErNi_5$. (I) Calculated for the parameters $x = 1.0$, $y = -0.10$, and CFOAS = 135 K; (II) calculated for the parameters $x = 1.0$, $y = -0.04$, and CFOAS = 135 K and (III) experimental (see text).

TABLE VI

SMOOTHED MOLAR HEAT CAPACITIES AND THERMODYNAMIC FUNCTIONS FOR $ErNi_5$

T(K)	C_p (J/mole K)	S (J/mole K)	$\left(\frac{H-H_0^0}{T}\right)$ (J/mole K)	$-\left(\frac{G-H_0^0}{T}\right)$ (J/mole K)
4.0	2.92	0.87	0.67	0.20
5.0	5.49	1.80	1.38	0.42
7.0	11.72	4.57	3.39	1.18
8.0	15.70	6.37	4.65	1.72
8.4	17.04	7.17	5.21	1.96
9.0	6.44	8.07	5.73	2.34
10.0	5.04	8.63	5.69	2.94
15.0	7.14	10.94	5.71	5.23
20.0	10.77	13.44	6.48	6.96
25.0	16.03	16.42	7.88	8.55
50.0	46.08	36.65	19.39	17.26
75.0	74.37	60.86	33.15	27.71
100.0	95.94	85.38	46.30	39.08
125.0	111.61	108.56	57.87	50.69
150.0	123.17	129.98	67.84	62.14
175.0	131.65	149.64	76.38	73.26
200.0	137.97	167.65	83.70	83.95
225.0	142.80	184.19	90.01	94.18
250.0	146.58	199.44	95.49	103.95
273.15	149.35	212.55	99.94	112.61
298.15	151.56	225.73	104.18	121.55
300.0	151.69	226.67	104.47	122.19

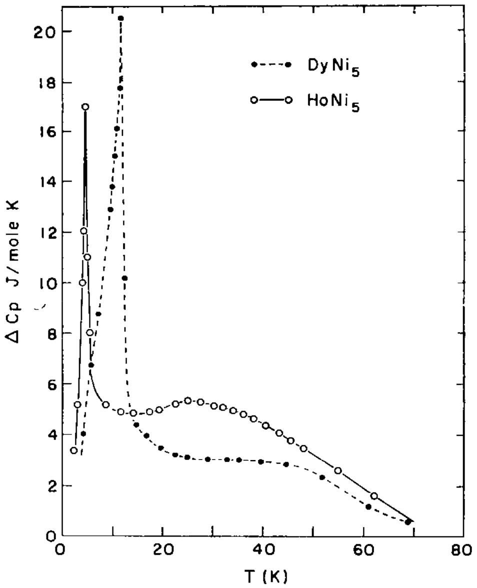

FIG. 5. Excess heat capacity vs temperature for $DyNi_5$ and $HoNi_5$ (●——) $DyNi_5$; (○——) $HoNi_5$.

the heat capacity measurements were made in the absence of an external field.

The "magnetic" contribution to C_p is obtained by subtracting the nonmagnetic contribution (C_{nm}) from the total. ("Magnetic" as used here includes both the contributions arising from the

TABLE VII

CRITICAL TEMPERATURES AND MAGNETIC ENTROPIES OF $LnNi_5$

Compound	Transition temp. (K) Magnetic study	Transition temp. (K) Thermal study	Magnetic entropy at 300 K (J/mole K)	Remarks	Ref.
$LaNi_5$	—	—	—	weak Pauli paramagnet	(*1*)
$CeNi_5$	<4 (?)	<4 (?)		Complex	(*1*, *7*)
$PrNi_5$	—	16, 58	16.9	Van Vleck paramagnet; exhibits two Schottky peaks	(*2*, *7*)
$NdNi_5$	13	6.4, 50	18.2	Peaks in heat capacity correspond to Curie temperature and maximum in the Schottky anomaly	(*1*, *7*)
$GdNi_5$	33	29.8, 30.6	14.9	Two peaks associated with onset of magnetic ordering in two stages	(*1*, *7*)
$DyNi_5$	15	12.0, 35.0	17.0	Peaks in heat capacity correspond to Curie temperature and maximum in the Schottky anomaly	(*6–8*) and present work
$HoNi_5$	23	4.1, 26.0	18.8		
$ErNi_5$	13	8.0, 30.0	17.1		

break-up of magnetic order and that originating with excitation within the crystal field spectrum.) C_{nm} is comprised of the electronic and vibrational components; it is commonly obtained experimentally by use of a nonmagnetic counterpart of the magnetic compounds under examination, $LaNi_5$ in this instance. If C_p of the nonmagnetic counterpart compound accurately represents C_{nm}, its C_p and that of the magnetic compounds become identical at higher temperatures where the magnetic entropy is fully developed. In the present instance C_p for $LaNi_5$ exceeds C_p for the magnetic compounds at higher temperatures and hence it does not accurately represent C_{nm}. Accordingly we have used a "rescaled" value of the $LaNi_5$ heat capacity. A factor f is found which will bring C_p for $LaNi_5$ and $DyNi_5$ into coincidence for $T \approx 300$ K. C_p for $LaNi_5$ at all temperatures is multiplied by this factor to give an improved estimate of C_{nm}. A corresponding procedure is used for $HoNi_5$ and $ErNi_5$. The magnetic contributions to C_p are plotted in Figs. 4 and 5 for the temperature region 2 to 70 K.

We note that there is excess heat capacity above the Curie temperature. This is a consequence of the importance of the crystal field interaction relative to exchange. The destruction of ferromagnetism occurs within one or more pairs of low-lying crystal field states. Excitation into the higher crystal field states occurs above T_c, giving rise to the higher temperature thermal anomalies. In this respect the three compounds involved in the present study behave in a fashion similar to $NdNi_2$ (*10*) and $CeIn_3$ (*11*).

The excess entropies evaluated by integrating $\Delta C_p/T$ up to 300 K are also included in Table VII. It is clear that these values are, in general, short of $R\ln(2J+1)$ by approximately $R\ln 2$. This is surprising since we expect an entropy of $R\ln(2J+1)$ if the system is magnetically ordered at low temperatures. The exchange field removes any degeneracy in the ground state. However, a residual entropy of $R\ln 2$ would occur if the relative strengths of the crystal field and exchange interactions were such as to produce two states with energies differing by less than 1 or 2 K. In the following paragraphs we examine the possibility that such a situation could occur. For the sake of brevity, we shall illustrate the details of calculation for only $ErNi_5$. However, the treatment is of general applicability and could readily be extended to the cases of $DyNi_5$ and $HoNi_5$, with only a few modifications in the details of the model.

In 1963, Bleaney (*12*) reported that in $LnNi_5$ compounds the major contribution to the crystal field interaction arises from the second-order term ($B_2{}^0$) and that the sign of $B_2{}^0$ determines the anisotropy of the rare earth ion in the ordered state. For example, if $B_2{}^0$ is positive, as in $HoNi_5$, the moments align themselves perpendicular to the c-axis and if $B_2{}^0$ is negative, as in $ErNi_5$, the moments tend to lie along the c-axis. Experimental evidence from neutron diffraction studies on $ErNi_5$ (*13*) and $TbNi_5$ (*14*) and also the recent theoretical treatment of Greedan and Rao (*15* on rare earth–cobalt systems indeed substantiate Bleaney's conclusion.

The moments of Er in $ErNi_5$ and hence the exchange field are directed along the c-axis. Under these conditions, the Hamiltonian acting on the rare earth ion in the ordered state is expressed as:

$$\mathcal{H} = g\mu_B J_z H_{ex} + \sum_{n=0}^{\infty} \sum_{m=n}^{-n} B_n{}^m O_n{}^m, \qquad (1)$$

in which the first term describes the influence of the exchange field and the second term is the generalized form of the crystal field contribution. As pointed out in earlier papers (*12*, *16*), symmetry considerations greatly reduce the number of terms in the crystal field part of the above Hamiltonian. For convenience in the calculation, the expression (1) is customarily reduced to (*16*):

$$\mathcal{H} = g\mu_B J_z H_{ex} + W_{246}\left[(1-|y|)\frac{O_2}{F_2} + xy\frac{O_4}{F_4} + y(1-|x|)\frac{O_6}{F_6}\right] \qquad (2)$$

where W_{246} is proportional to the crystal field overall splitting (CFOAS), x and y describe the relative importance of fourth-order to sixth-order and fourth-order to second-order contributions, respectively, and $O_6 = O_6{}^0 + 5.66\,O_6{}^6$. The constant 5.66 is the value calculated on the basis of the point charge model. All other terms in the above expression have their usual significance (*16*). We note that nickel is regarded as neutral and hence does not contribute to the crystal field acting upon the Er^{3+} ion. The electrical neutrality of nickel occurs because of electron transfer from Er to Ni to fill the Ni $3d$ shell (*17*). This is expected on general grounds and is borne out experimentally by the neutron diffraction work of Corliss and Hastings (*13*), who find nickel in $ErNi_5$ to be nonmagnetic. The exchange field,

H_{ex}, is calculated from simple molecular field theory (*18*) as follows:

$$H_{ex} = \frac{3k}{g\mu_B} \cdot \frac{T_c}{(J+1)}, \qquad (3)$$

where T_c is the Curie temperature, k is the Boltzmann constant, μ_B is the Bohr magneton and g is the Landé factor. The Hamiltonian in Eq. (2) was solved using standard procedures (*2*, *16*) to obtain eigenvalues, eigenfunctions and moments; a number of selected combinations of the parameters W_{246}, x and y were utilized.

As a first-order approximation, the contribution to the Hamiltonian in Eq. (2) from the sixth-order term was neglected as justified from point charge model calculations. This fixes the values of x to be equal to 1.0. The value of W_{246} is obtained by matching the peak temperature of the calculated Schottky heat capacity to that obtained experimentally.

In Fig. 6 we display the eigenvalues of the states obtained as a function of y for the selected combinations of x and CFOAS. It is clear from Fig. 6 that if y is either -0.04 or -0.10 there are two low-lying levels. If such a situation exists, the magnetic entropy obtained at 300 K is explainable.

The eigenvalues were computed for the combinations of x, y and CFOAS as described above for the paramagnetic region. Using these eigenvalues, we have evaluated the Schottky heat capacity from the expression:

$$C_{\text{C.F.}} = \frac{R}{T^2}\left(\frac{d^2 \ln Q}{d(1/T)^2}\right), \qquad (4)$$

where $Q = \sum_i \exp(-E_i/kT)$.

The heat capacity results thus obtained for the two combinations of y are compared with experimental values in Fig. 4. For $y = -0.10$ the agreement appears to be reasonably satisfactory, particularly in view of the approximations entailed in setting up the Hamiltonian and in estimating the lattice heat capacity. The eigenvalues, eigenfunctions and moments of the states are presented in Table VIII.

We add that calculations were made based on point charge model considering only two axial and six equatorial rare earth neighbors around the reference rare earth ion. These calculations gave a value for $y = -0.08$ which is in close agreement with that deduced from the heat capacity data.

One additional feature of these systems merits comment. Assuming that exchange is due to the RKKY interaction and the molecular field theory applies, de Gennes showed (*19*) some years ago that T_c is proportional to $(g-1)^2 J(J+1)$, the

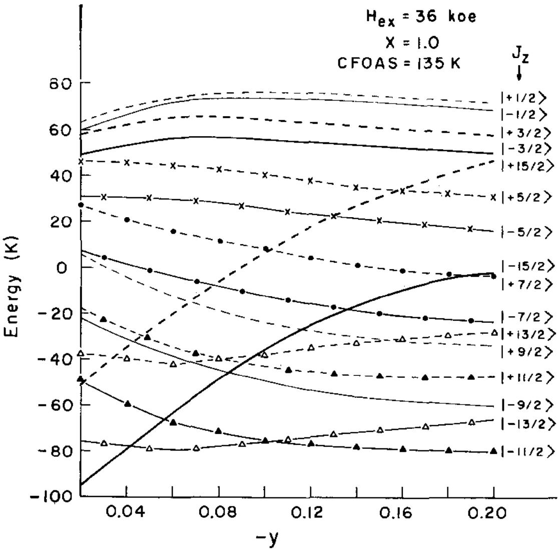

FIG. 6. Variation of eigenvalues of various levels as a function of y for $ErNi_5$ ($x = 1.0$, CFOAS = 135 K and Exchange field = 36 kOe).

TABLE VIII

CHARACTERISTICS OF THE CRYSTAL FIELD STATES OF Er^{3+} IN $ErNi_5$[a]

Energy	Eigenfunction	Magnetic moment[b]
77.3	|1/2⟩	0.0667
74.4	|−1/2⟩	−0.0667
64.95	|3/2⟩	0.2000
56.25	|−3/2⟩	−0.2000
40.1	|5/2⟩	0.3333
25.6	|−5/2⟩	−0.3333
8.0	|7/2⟩	0.4667
7.4	|15/2⟩	1.0000
−12.3	|−7/2⟩	−0.4667
−23.4	|9/2⟩	0.6000
−36.1	|−15/2⟩	−1.0000
−38.3	|13/2⟩	0.8667
−43.2	|11/2⟩	0.7333
−49.5	|−9/2⟩	−0.6000
−75.1	|−11/2⟩	−0.7333
−76.0	|−13/2⟩	−0.8667

[a] In the ordered state.

[b] As a fraction of gJ, the free ion moment in Bohr magnetons.

so-called de Gennes function. If so, T_c for the three compounds studied should be in the ratio 12.0:6.9:4.3 K for the Dy, Ho and Er compounds, respectively. Actually T_c is in the ratio 12.0:4.1:8.0 K (see Table VII). Clearly in these systems proportionality with the de Gennes function is not observed. This may be due to the neglect of crystal field effects in de Gennes' treatment or the inadequacy of other postulates involved in his treatment or both. The strength of the crystal field interaction is comparable with exchange and hence it is perhaps unrealistic to expect a treatment which neglects it to conform with experiment.

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