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Low-Temperature Heat Capacity Studies on $DyFe_3$, $DyCo_3$, $DyNi_3$, and $LaNi_3$*

K. S. V. L. NARASIMHAN, R. A. BUTERA, R. S. CRAIG, AND W. E. WALLACE

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

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Low-temperature heat capacity measurements were made on $DyFe_3$, $DyCo_3$, $DyNi_3$, and $LaNi_3$ over the temperature range 1.4–15°K. Two anomalies, observed at 1.8 and 9.3°K, are ascribed to the presence of an oxide and a hydride. Another anomaly exists at 3.2°K, which may be due to hydroxide. The observed electronic specific heat coefficients are interpreted in terms of the band structure of these materials.

Introduction

The magnetic properties of rare earth intermetallics have been of interest in recent years, partly because of the promise of these intermetallics for practical applications (*1*). In this general connection, studies have been made of the ternary systems $DyFe_{3-x}Ni_x$, $DyCo_{3-x}Ni_x$, and $DyFe_{3-x}Co_x$. Measurements of saturation magnetizations (*2*, *3*) and the Fe hyperfine field (*4*) (by Mössbauer spectroscopy) revealed a number of unusual features. It appeared that information in regard to the band structure of these materials would facilitate interpretation of the observed magnetic properties. To obtain such information, i.e., the electronic specific heat coefficient (γ) and the density of states at the Fermi level, specific heats of these materials were determined in the range 1.5–15°K.

Usually, the γ and the density of states can be obtained in a straightforward way from such measurements. However, in the case of rare earth systems, complications frequently arise (*5*, *6*) because of the influence of impurities. The work reported in this paper was undertaken with two objectives in mind: (1) to clarify the role of impurities in regard to the heat capacity of rare earth systems, and (2) to obtain γ and the density of states for $DyFe_3$, $DyCo_3$, $DyNi_3$, and $LaNi_3$.

Experimental

The samples (mass ~ 5 g) were prepared by melting together stoichiometric proportions of the metals in an inert atmosphere in a cold boat and then annealing the alloy wrapped in tantalum foil in an evacuated quartz tube for 1 week at 950°C. The dysprosium and lanthanum used were stated by the manufacturer (Research Chemicals) to have a purity of 99.9%; more than 90% of the impurity was reported to be tantalum. These figures refer only to solid impurities; no information was given concerning gases. The nickel, iron, and cobalt (Johnson–Matthey spectrographically standardized grade) had a stated purity of 99.999%; the principal contaminants were copper, iron, and silicon. X-ray diffraction measurements on powder specimens were carried out employing a General Electric XRD-3 diffractometer using Mo$K\alpha$ radiation. All the lines observed could be indexed to the $PuNi_3$ type of structure. The lattice parameters were obtained by a least squares refinement of the observed 2θ values and are shown in Table I.

Heat capacity measurements were carried out in the temperature range $T = 1.4$–15°K. A computer-controlled calorimeter was used in which energy was supplied to the sample in pulses (1-sec duration from 1.4 to 4.2°K, 10-sec

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TABLE I

HEAT CAPACITY DATA FOR $DyFe_3$, $DyCo_3$, AND $LaNi_3$

Composition	Lattice parameters[a]		$\gamma \times 10^2$ (joules mole^{-1} deg^{-2})	β (joules mole^{-1} deg^{-4})	$N(E_F)$ States (eV/atom)	θ_D (°K)
	a (Å)	c (Å)				
$DyFe_3$	5.12	24.58	2.58 ± .03	2.21 ± .07	2.73	328
	(5.120)	(24.56)[b]				
$DyCo_3$	5.01	24.36	4.71 ± .06	7.66 ± .06	4.99	217
	(4.995)	(24.36)[c]				
$LaNi_3$	5.10	25.04	1.63 ± .05	5.86 ± .02	1.73	237
	(5.086)	(25.01)[d]				
$DyNi_3$	4.97	24.14	—	—	—	—
	(4.964)	(24.16)[e]				

[a] Numbers in parentheses refer to the values reported in the literature.
[b] See Ref. *7*.
[c] See Ref. *8*.
[d] See Ref. *9*.
[e] See Ref. *10*.

4.2 to 15°K) and measured by an integrating digital voltmeter. Control of the experiments (pulsing and determination of temperature equilibria), data acquisition (measurement of temperatures and energy inputs), computation, and display of the final results were carried out automatically. Fuller details of the calorimetric procedure will be published in another paper (*11*). From the lowest temperature to 4.2°K, points were taken every ~0.12°K, above 4.2°K every ~0.2°K. Each heat capacity run involved at least three passes over the whole temperature range, giving a total of more than 150 points. The precision at all temperatures was better than 1 %.

Results

Figures 1–3 show the variation of heat capacity as a function of temperature for all the compounds investigated. Since the magnetic ordering temperatures are 600°K for $DyFe_3$ and 450°K for $DyCo_3$, the magnetic contribution to the heat capacity should be small, probably negligible, at the temperatures involved in the present work. However, for $DyNi_3$ with a T_c of 66°K, magnetic contribution to the heat capacity is likely to be appreciable. At low temperatures, if the heat capacity is due only to vibrational and electronic contributions, then the heat

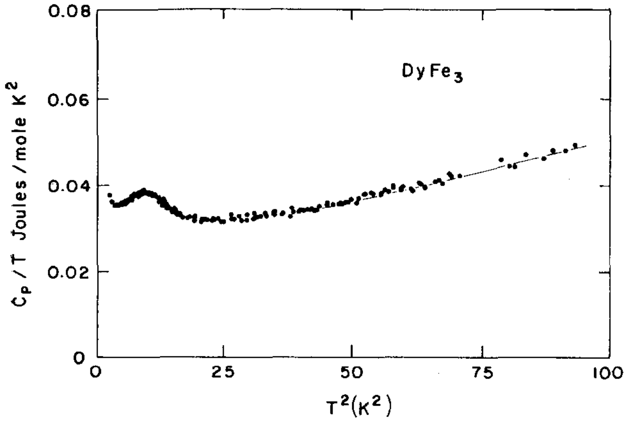

FIG. 1. C_p/T_3 vs T^2 for DyFe.

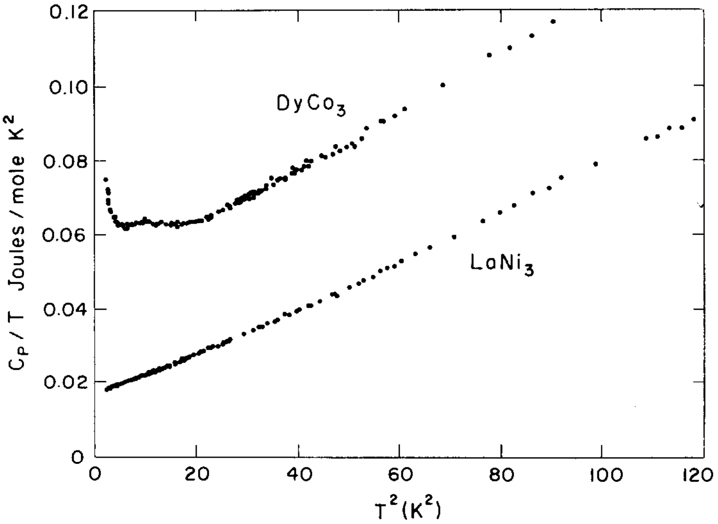

FIG. 2. The specific heat of DyCo$_3$ and LaNi$_3$.

capacity may be expressed as $C_p = \gamma T + \beta T^3$, where γ is the electronic heat capacity coefficient and βT^3 is the lattice contribution to the heat capacity. A plot of C_p/T vs T^2 should be a straight line with a slope of β and intercept of γ. As seen from Figs. 1–3, except for LaNi$_3$, the compounds showed anomalies in the low temperature heat capacity. This materially complicates evaluation of γ and β. Before pursuing the evaluation of γ and β, the cause of these anomalies should be clarified.

Three anomalies are observed: (a) a weak maximum in the heat capacity at $T = 3.2$°K, (b) a broad hump between about 9.3 and 9.7°K, and

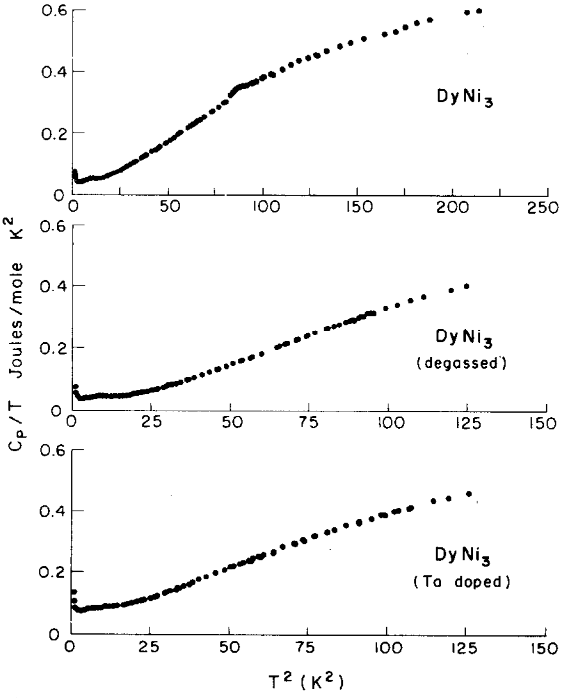

FIG. 3. Specific heat of DyNi$_3$. Top: the "virgin" sample. Middle: degassed sample. Bottom: tantalum-doped sample.

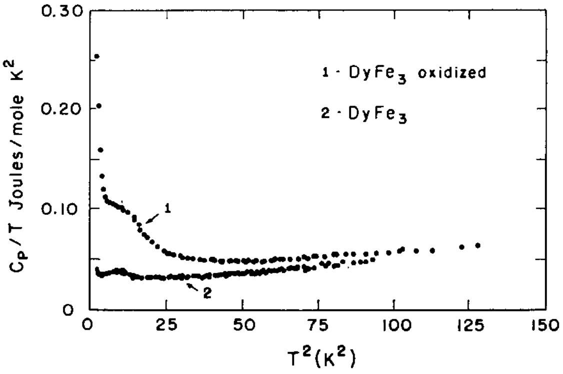

FIG. 4. C_p/T vs T^2 for $DyFe_3$ (oxidized) and original sample.

(c) at the very lowest temperatures ($T < 1.8$°K) a sharp increase in the heat capacity with decreasing temperatures. Anomalies (a) and (c) are observed in all the compounds; anomaly (b) is observed only in the case of $DyNi_3$. We feel that these are all impurity effects.

The most likely impurities are deemed to be hydrogen, oxygen, and tantalum. Commerically available rare earths frequently contain appreciable amounts of dissolved hydrogen (*12*). Alloys containing rare earths generally react rather readily with oxygen from the air, and so the presence of small amounts of oxides can be expected. Tantalum is usually the chief metallic impurity in rare earths, being dissolved from the metal crucibles used in the preparation process. To ascertain whether any of these anomalies were caused by hydrogen, $DyNi_3$ was degassed at 1000°C in ultrahigh vacuum until the residual pressure fell to 2×10^{-9} Torr for the hot metal. Hydrogen was evolved in a quantity equivalent to ~2 atomic %. Identification of the gas and the method of estimating its volume are described elsewhere (*13*).

C_p/T vs T^2 for the degassed specimen is shown in Fig. 3. We note that the heat capacity of the material has decreased over the entire temperature range (at higher temperatures by as much as 15%), and the hump at 9.5°K has disappeared; the linear portion of the curve has been significantly extended. The overall reduction in heat capacity is probably due to the removal of interstitial hydrogen; the disappearance of the hump is probably caused by the removal of dysprosium hydride. Susceptibility data (*14*) show that DyH_2 has a Néel point at about 8°K. (Since the Néel temperature is known to vary with the applied field, magnetic data will yield a lower temperature for magnetic ordering of DyH_2.)

As it would have been difficult to reduce any oxides present in the specimen without the risk of introducing other contaminants, it was decided to determine whether any of the anomalies correlated with the presence of oxygen by intentionally allowing the metal to react with oxygen. The sample of $DyFe_3$ was heated in an oxygen atmosphere at 800°C for 30 min. The samples picked up 0.6 wt% oxygen. Measurements then showed the abrupt rise in heat capacity (decreasing T) at very low temperatures to be greatly accentuated (Fig. 4). The anomaly is probably the tail of a heat capacity peak centered at 1.2°K, at which temperature Dy_2O_3 is reported to become antiferromagnetic (*15*).

The most likely sources of the third anomaly at 3.2°K appeared to be dissolved tantalum, which at 4.4°K becomes superconducting (*16*), or traces of dysprosium hydroxide $Dy(OH)_3$, which has a Curie point at 3.5°K (*17*). Since there was no obvious way of removing the tantalum, and since the maximum had not been affected by either of the previous treatments, the only way of gaining information about the cause of this anomaly seemed to be to increase the amount of tantalum. A known weight of tantalum was added to the degassed sample to considerably increase the impurity level. Preparation of this compound, $DyNi_3Ta_{.045}$, was accomplished by melting the sample and Ta in a cold boat. After annealing and further degassing, heat capacity measurements were made. The results are shown in Fig. 3. The heat capacity has been increased by a (virtually) constant amount over the whole temperature range, and, at 3.2°K, this increment is one of almost 100%, but the size of the anomaly remains substantially unchanged. Hence, the

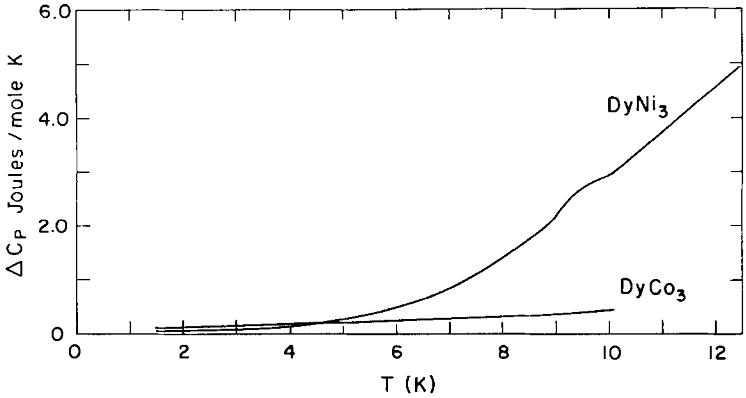

FIG. 5. A plot of difference between the heat capacity of $DyNi_3$, $DyCo_3$ and $LaNi_3$.

anomaly is probably due to $Dy(OH)_3$, and the only effect of the tantalum is an overall enhancement of the heat capacity.

X-ray examination of the degassed and tantalum-doped samples of $DyNi_3$ indicate no change in the crystal structure. Examination of the extremely high back reflections might reveal the effect of these impurities. No such attempts were made in the present case. Also, thermomagnetic analysis from 4.2°K to above room temperature does not show any extraneous phases. The Curie temperature of the virgin sample of $DyNi_3$ is unaffected by the degassing or tantalum doping. Thus, the presence of the impurities, in the present study, is more easily observed by heat capacity measurements than by the magnetic studies.

The presence of these anomalies makes the task of obtaining γ and β values difficult. This is true for all the compounds except for $LaNi_3$ which showed a normal behavior. In the case of compounds showing anomalies, there is a linear part of the plot of C_p/T vs T^2 between 4.8 and 9°K. Extrapolating from this region yields the values of γ and β shown in Table 1. The Debye temperature θ is estimated from the relation

$$\beta = (12/5)\pi^4 k_\beta L/\theta,$$

and the averaged density of states at the Fermi surface $N(E_F)$ from

$$\gamma = (\pi^2/3)k_\beta{}^2 N(E_F),$$

where L is the number of atoms per mole, and k_β is the Boltzmann constant.

The procedure described in the preceding paragraph yields a negative γ for $DyNi_3$. This is undoubtedly due to the importance of the magnetic contribution to the heat capacity. This is large compared to the contribution for $DyCo_3$ and $DyFe_3$ because of the low Curie temperature of $DyNi_3$. ΔC_p, the difference between C_p for $DyNi_3$ and $LaNi_3$, should indicate the magnitude of the magnetic heat capacity. Figure 5 shows the plots of ΔC_p vs T for $DyNi_3$ and $DyCo_3$.

Due to the difficulties in obtaining the γ value for $DyNi_3$, we assume $LaNi_3$ to represent a good substitute. The validity of this assumption is based on the facts that (a) the two compounds are isostructural, and (b) both Dy and La donate the same number of electrons to the 3*d* band of nickel. By taking $LaNi_3$ to simulate magnetic $DyNi_3$, we are neglecting the polarization effect of dysprosium spins, and, in addition, we assume that the γ of $LaNi_3$ is not enhanced by proximity of the *f* electron energies to the Fermi energy. We now discuss the variation of γ as dysprosium is alloyed with different transition metals; γ increases going from $DyFe_3$ to $DyCo_3$ and is small at $LaNi_3(DyNi_3)$. The γ value for the cobalt compound is nearly twice that of $DyFe_3$ and nearly three times that of $LaNi_3(DyNi_3)$. Since the nickel band is nearly full in the compound $LaNi_3(DyNi_3)$, we would expect a lower value for γ as compared to that for $DyCo_3$ or $DyFe_3$. In elemental iron, there are 2.9 holes in the 3*d* band and in cobalt 2.0 holes (*18*). However, during compound formation, the electrons from dysprosium will fill part of the holes. If the number of electrons donated by the rare earth is the same in $DyFe_3$ and $DyCo_3$, superficially we might expect the γ value to be higher for $DyFe_3$. We observed the reverse situation.

This apparent contradiction can be reconciled if one considers the details of the band structure (*18*). In the case of iron there are 2.6 holes in the spin-down band and 0.3 holes in the spin-up band, and the spin-down band Fermi level remains at the minimum of the density of states as long as there are holes in the spin-up band. Once the spin-up band is fully populated, electrons will enter the spin-down band, and the spin-down band Fermi level will move out of the minimum. The valence electrons of the rare earth partly fill the spin-up band in $DyFe_3$, and the density of states as measured will be small because the spin-up band is almost full and makes only a small contribution to γ. On the other hand, in $DyCo_3$, the spin-up band is fully populated and only the spin-down band participates in electronic conduction. Because of the high density of states of the spin-down band, the γ value observed for this compound is higher. Further support to the statement that in $DyFe_3$ the spin-up band is not saturated is obtained from Mössbauer measurements on $DyFe_{3-x}Ni_x$ (*4*). The hyperfine field increases as nickel is substituted for iron up to $x = 0.5$ and decreases on further increasing x. This is because as x is increased beyond 0.5, the spin-down band population increases, the net moment decreases, and hence the hyperfine field.

Although the observed variation in γ is consistent with a band model of these compounds, we note that the values of γ are influenced by the impurities in the compounds. Preliminary heat capacity measurements on isostructural $YFe_{3-x}Ni_x$ compounds suggested that the sub-bands in YFe_3 are not saturated. In these compounds, no anomalies were seen in the low-temperature heat capacity, and, hence, definite conclusions can be drawn from the γ values. Magnetic and Mössbauer measurements on these compounds are in progress.

Conclusion

The present work shows that the small amounts of hydrogen and tantalum, which are almost always present in commercially available rare earths, can cause significant changes in the low-temperature heat capacities of the metals and of alloys made from them. Important changes have also been shown to be caused by the oxides and possibly hydroxides that may be formed during sample preparation and handling. It is clear that if reliable values of electronic and lattice heat capacities are to be obtained, great care must be exercised to use metals of very high purity, and to exercise precautions in preparing and treating samples to eliminate gaseous contaminants. The work also points to the need for employing more caution in analyzing existing heat capacity data. The observed values of γ for $DyCo_3$, $DyFe_3$, and $LaNi_3$ can be interpreted on the basis of a band model of transition metal atoms. In the case of $DyNi_3$, large excess heat capacity was observed arising possibly from the magnetic contribution. Further studies of the heat capacity of solid solutions of $DyFe_{3-x}Co_x$ and $DyFe_{3-x}Ni_x$ compounds are being made to obtain the details of the band structure in these compounds.

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