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Magnetic Characteristics of Some Ternary Intermetallic Compounds Containing Lanthanides*

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Magnetic characteristics are given for the five ternary systems $Ln_xLn'_{1-x}Co_5$ with the combinations Gd and Nd, Dy and Pr, Dy and Nd, Gd and Dy, and Gd and Ho, and for the ternary Dy $(Co_xNi_{1-x})_5$. Curie temperatures (T_c) of the Ln–Ln′–Co ternaries range from 912 to 1008°K. Replacement of Co by Ni in $DyCo_5$ decreases T_c to 63°K in $DyCoNi_4$. Magnetization-temperature and the magnitude of saturation moment indicate the Ln–Ln′–Co ternaries to be ferrimagnets; the Ln–Co (or Ln′–Co) coupling is ferromagnetic when Ln = Pr or Nd and antiferromagnetic when Ln = Gd, Dy, or Ho. The magnetic behavior of the Dy–Co–Ni ternaries indicates that they are also ferrimagnetic. Ni in these ternaries unlike Ni in $DyNi_5$ is magnetic. The moments indicate a nickel moment ranging from 0.16 to 0.49 μ_B per atom and with Dy coupled antiparallel to Ni and Co.

I. Introduction

Previous publications emanating from this laboratory have provided magnetic information, including the nature of the coupling, for a number of ternary systems containing lanthanides (*1–4*). Studies of the ternaries $Ln_xLn'_{1-x}Al_2$, $Ln_xLn'_{1-x}Ni_2$, and $Ln_xLn'_{1-x}Ni_5$ (Ln and Ln′ represent two different lanthanides) have shown the Ln–Ln′ spin coupling to be ferromagnetic in all cases. As a consequence, since the L, S coupling is $L-S$ for the light lanthanides and $L+S$ for the heavy lanthanides, the Ln, Ln′ coupling is ferromagnetic when both lanthanides are heavy or light and is antiferromagnetic when one is heavy and the other is light.

In the three ternary systems cited in the previous paragraph, the lanthanides are in chemical union with a nonmagnetic partner. It was not clear when the present study was initiated whether the systematization found for these ternaries would apply when the partner is magnetic. To answer this question measurements were undertaken on a series of ternaries represented by the formula $Ln_xLn'_{1-x}Co_5$. Shidlovsky and Wallace studied (*3*) the ternaries $LnCo_{5-x}M_x$ with M = Cu and Al in the hope of inducing a reversal of coupling by partial replacement of cobalt; these efforts were unsuccessful. As an extension of this work results are now presented on Dy $(Co_xNi_{1-x})_5$ the substituent for cobalt in this case being a transition metal.

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II. Experimental Details

The procedures employed followed closely those used in the earlier study (*1*). The lanthanides were the best-grade materials available commercially (99.9% with respect to other metals); they were obtained from Research Chemicals. The cobalt and nickel used were spectroscopic standard grade (99.999%) obtained from the Johnson–Matthey Co. The ternaries were formed by levitation melting. X-ray patterns of the as-cast material confirmed the $CaCu_5$ structure in all cases. Selected samples were heat treated with little effect on either the quality of the diffraction patterns or the magnetic results.

The magnetic measurements were made over the temperature range 4–1000°K using a technique that is now standard in this laboratory. The Faraday method was used with an automatic recording balance that has been described (*5*).

III. Results and Discussion

The results are largely summarized in Table I and in Figs. 1–5. It is well known that the magnetization-temperature curves of ferrimagnetic materials

TABLE I

MAGNETIC CHARACTERISTICS OF $Ln_xLn'_{1-x}Co_5$ TERNARIES

x	Magnetic moment (μ_B/formula unit) Meas.	Calc.[a]	T_c (°K)
	$Gd_xNd_{1-x}Co_5$		
0.0 ($NdCo_5$)	11.7	11.8	910[b]
0.2	8.5	9.7	950
0.4	7.0	7.7	965
0.6	5.6	5.6 (14.0)	1000
0.8	3.2	3.2	1000
1.0 ($GdCo_5$)	1.3[b]	1.5	1008[b]
	$Dy_xPr_{1-x}Co_5$		
0.0 ($PrCo_5$)	10.0	11.7	912[b]
0.2	8.0	9.1	955
0.4	5.7	6.4	955
0.6	3.3	3.8 (14.0)	960
0.8	1.36	1.14	975
1.0 ($DyCo_5$)	1.6[b]	1.5	966[b]
	$Dy_xNd_{1-x}Co_5$		
0.2	8.6	9.2	920
0.4	7.8	6.5	930
0.6	7.3	3.9 (15.8)	940
0.8	1.6	1.2	950
0.85	0.8	1.0	—
0.9	0.5	0.2	—
	$Gd_xDy_{1-x}Co_5$		
0.2	0.89	0.90	1000
0.4	0.54	0.30	1000
0.6	0.47	0.30 (16.7)	1000
0.8	1.12	0.90	1005
	$Gd_xHo_{1-x}Co_5$		
0.0 ($HoCo_5$)	1.9[b]	1.5	1000[b]
0.2	1.02	0.90	1010
0.4	1.25	0.30	1010
0.6	1.39	0.30 (16.7)	1015
0.8	1.57	0.90	1010

[a] Calculated assuming the coupling scheme described in the text. Moments used (μ_B/atom): Co, 1.7; Pr, 3.2, Nd, 3.27; Gd, 7.0; Dy and Ho, 10.0. The numbers in parenthesis at the $x = 0.6$ composition give the magnetic moment for ferromagnetic coupling of all three species.

[b] Taken from the review in Ref. (*6*).

deviate substantially from the Brillouin curve exhibited by ferromagnetic substances. This is evident for the several ternaries studied, all of which (with the possible exception of $DyCoNi_4$) appear to be ferrimagnetic. The data shown in Figs. 1–4 are illustrative. Compensation points and maxima in the magnetization-temperature curves which can occur with ferrimagnetic materials are evident.

The measured saturation moments for the $Ln_xLn'_{1-x}Co_5$ ternaries are given in column 2 of Table I. In column 3 are presented moments calculated on the basis of the coupling scheme observed (*1*, *2*) for $LnCo_5$ binaries and ternaries involving lanthanides combined with Ni and Al, namely:

1. The heavy lanthanides (Gd, Dy, Ho) couple antiparallel to cobalt;
2. the light lanthanides (Pr, Nd) couple parallel to cobalt;
3. the heavy–heavy and heavy–light coupling is parallel and antiparallel, respectively.

For simplicity, this is termed the ferrimagnetic coupling scheme. The moment calculated for all three species coupled parallel is shown for $x = 0.6$ in each case. It is clear that the first, i.e., the ferrimagnetic, coupling scheme agrees much more closely with experiment than the one involving ferromagnetic coupling. Even so there are substantial deviations between the calculated and measured values for ternaries containing light lanthanides. It appears that the deviations largely originate with the variable moment of cobalt and the light lanthanide component.

Bleaney (*7*) first drew attention to the likelihood that the size of the cobalt moment was a function of the nature of the lanthanide element with which it was united; the exchange field of the lanthanide was presumed to produce a substantial induced component to the cobalt moment. The postulate of a variable cobalt moment was later confirmed (*8*, *9*) by neutron diffraction studies. More recently, Leon and Wallace (*4*) showed that the Pr^{3+} ion behaves similarly. Thus the assumption of fixed ionic moments for calculating the saturation magnetizations in Table I is valid only as a rough approximation. In this respect, it is to be noted that the calculational scheme used overestimates the moment of $PrCo_5$ by nearly 2 μ_B.

While variation in ionic moments seems to be the main influence in the deviation of computed and observed moments of most of the $Ln_xLn'_{1-x}Co_5$ ternaries studied, it does not appear to be the sole effect. The deviation noted for $Dy_{0.6}Nd_{0.4}Co_5$ seems to be too large to be reasonably ascribed to variation in the individual ion moments. It seems in this case as if the magnetic structure differs from that postulated. It is of interest to note that similar aberrations were observed (*2*) in the earlier studies

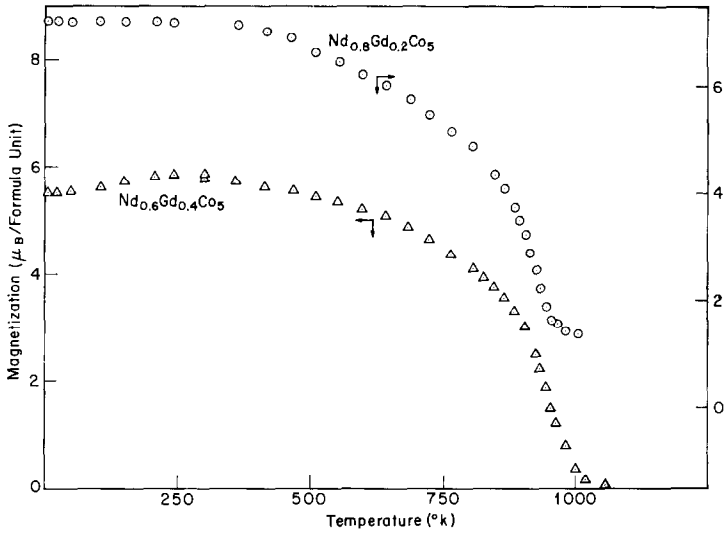

FIG. 1.

of $Ln_xLn'_{1-x}Ni_5$ ternaries with Ln = Nd and Ln′ = Ho.

The situation in regard to the $Ln_xLn'_{1-x}Co_5$ ternaries can be summarized as follows: Although agreement between computed and observed results is, in several cases, only fair, there is little reason to doubt the essential correctness of the coupling scheme postulated above, except for $Dy_{0.6}Nd_{0.4}Co_5$. The possibility that all species are ferromagnetically coupled can be excluded. These conclusions are supported not only by the magnitude of magnetic moments but also by the shape of the magnetization-temperature curves.

The curves shown in Fig. 4 for the Dy–Co–Ni ternaries display an interesting alteration of magnetic behavior. In $DyCo_5$ the magnetic properties are dominated except at the lowest temperatures, by the Co–Co interaction, giving rise to a Curie temperature of nearly 1000°K. The magnetic moment of Dy (10 μ_β) exceeds that of the 5 Co's (8.5 μ_β), giving a net moment of 1.5 μ_β (1.6 μ_β measured) at 0°K. The Dy moments are less strongly coupled so that with rise in temperature the magnetization of the Dy sublattice decreases more rapidly than that of the Co sublattice. This gives a minimum in magnetization at about 130°K, the so-called compensation point.

It is anticipated that as Co is replaced with Ni, which is either nonmagnetic or at least less strongly magnetic than Co, the coupling in the cobalt sublattice would be weakened and, hence, relatively

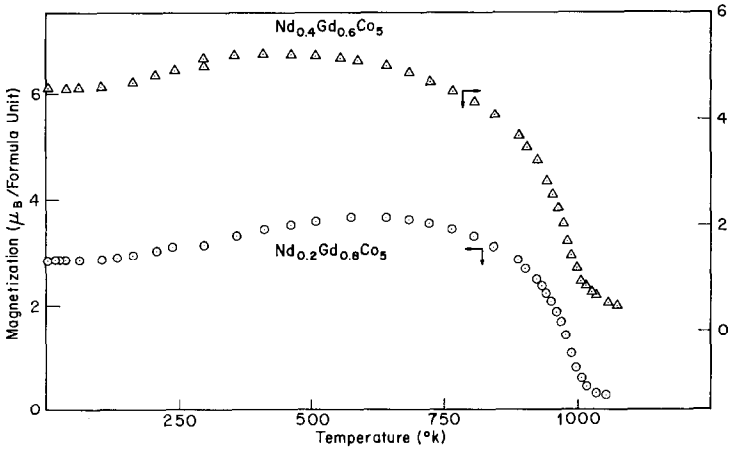

FIG. 2.

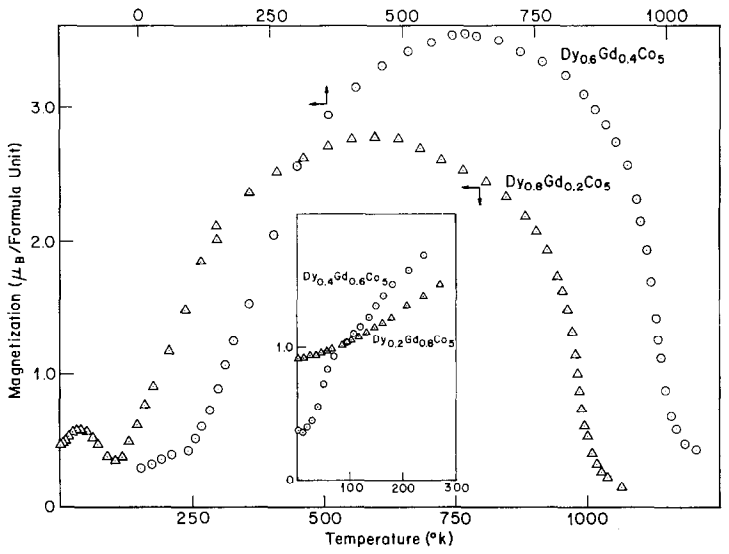

FIG. 3.

speaking, in the Dy sublattice strengthened. Consequently, a rise in compensation point is expected with increasing Ni content and this is indeed observed. Eventually the coupling of the Co sublattice will be weakened to the point at which it is comparable in strength with that in the Dy sublattice. Then the magnetic order in both sublattice will have identical susceptibility to destruction by rising temperature, the compensation point will disappear and the magnetization-temperature curve will resemble that of a normal ferromagnet. This is observed in $DyCoNi_4$ (Fig. 4). It exhibits a Curie temperature of about 60°K as compared with 17°K for $DyNi_5$, indicating that interactions in the Co–Ni sublattice are still dominant. In all, the magnetization vs temperature behavior of the Dy–Co–Ni ternaries changes in systematic and understandable ways.

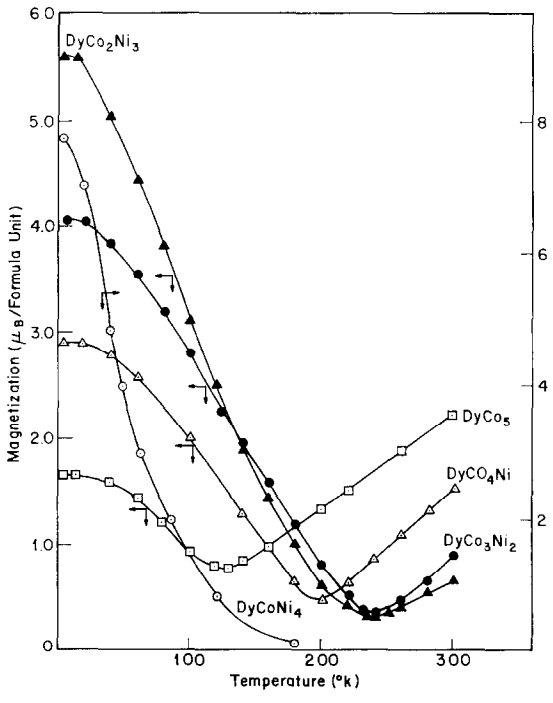

FIG. 4.

The saturation moments, corrected when necessary to 0°K, for the Dy–Co–Ni ternaries are shown in Fig. 5. The moments measured fall below those computed from a linear interpolation between the moments of the two binary compounds. Since Mössbauer work has indicated (*10*) a Dy moment within a few percent of that for the free tripositive ion in both $DyCo_5$ and $DyNi_5$, a constant moment of 10 μ_β in the ternaries can be safely assumed. To account for the discrepancy between the measured and linearly interpolated values it is necessary to ascribe either (1) a larger moment for Co in the ternaries than in $DyCo_5$ or (2) a larger moment for Ni in the ternaries than in $DyNi_5$, and to regard the two sublattices as antiferromagnetically coupled. The latter assumption seems reasonable as it is consistent with all earlier work on Dy–Co and Dy–Ni compounds (*6*, *11*). Postulate (1) seems unreasonable and is discarded. Postulate (2), implying that nonmagnetic nickel in $DyNi_5$ acquires

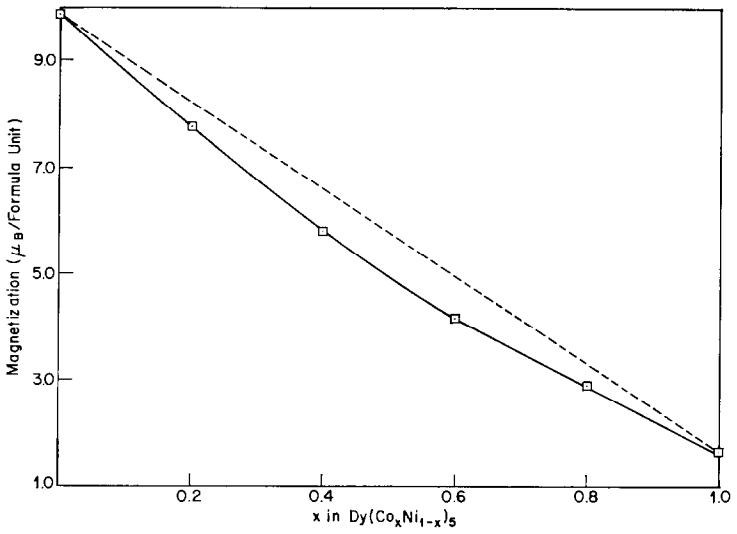

FIG. 5.

a moment when partially replaced by magnetic Co, seems entirely plausible. The nickel moment, estimated using $10\mu_\beta$ and $1.66\mu_\beta$ for Dy and Co, respectively, is given in Table II. The Co moment used is the value from the measured $DyCo_5$ moment. The acquisition of a moment for Ni in the ternaries when it lacks a moment in $DyNi_5$ is probably related to the factors which produce the variable cobalt moment in $LnCo_2$ compounds from 0 in YCo_2 to 1.7 in $GdCo_5$ or $DyCo_5$. The nickel moment in the Dy–Co–Ni ternaries is in the same range as that in the Ln_2Ni_{17} series, namely, about $0.3\ \mu_\beta$.

TABLE II

NICKEL MOMENT IN $Dy(Co_xNi_{1-x})_5$

x	Ni moment (μ_β)
0.0	0.00
0.2	0.16
0.4	0.33
0.6	0.49
0.8	0.47

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