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Magnetic Characteristics of Intermetallic Compounds Containing Two Lanthanides Combined with Nickel†

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Magnetic characteristics of four ternary Laves phase and four ternary Haucke phase systems represented by the formulas $Ln_xLn_{1-x}Ni_2$ and $Ln_xLn'_{1-x}Ln_5$, respectively, are reported. Ln–Ln′ combinations studied are: Gd–Dy, Gd–Ho, Gd–Nd and Ho–Nd, comprising two heavy–heavy and two heavy–light combinations. Saturation moments and Weiss constants (θ) indicate that the Ln–Ln′ spins always couple ferromagnetically, as in the $Ln_xLn'_{1-x}Al_2$ systems, for all cases except in the $Ho_xNd_{1-x}Ni_5$ system. The measured saturation moments are inconclusive for this system. However, from the temperature dependence of magnetization this system appears to be antiferromagnetic as expected from the systematics of the spin coupling observed for related ternaries.

Curie–Weiss (C–W) behavior with paramagnetic moments in good agreement with free-ion values is exhibited by all systems except $Gd_xNd_{1-x}Ni_5$. Large departures from C–W behavior and large negative Weiss constants are noted for this system. These are ascribed to interactions with the crystal field. The crystal field interaction is more important in $Gd_xNd_{1-x}Ni_5$ than in $Ho_xNd_{1-x}Ni_5$ implying significantly different conduction electron behavior in these materials.

The magnetic behavior of the Haucke phases is less ideal than the Laves phases, presumably due to the higher Ni concentration in the former and the greater likelihood that Ni is involved in the magnetic interactions.

I. Introduction

The magnetic characteristics of a number of Laves phase ternary systems represented by the formula $Ln_xLn'_{1-x}Al_2$ have recently been reported (*1*). (Ln and Ln′ represent two different lanthanides.) In keeping with earlier findings by Williams *et al.* (*2*) it was established that the spin coupling of the lanthanides is always ferromagnetic. Since the L–S coupling for light and heavy lanthanides is opposite, it follows that the ternaries in which Ln and Ln′ are both light or both heavy are ferromagnetic but in ternaries containing one light and one heavy lanthanide the Ln–Ln′ coupling is antiferromagnetic. The present investigation was undertaken to ascertain whether a similar systematization holds for the corresponding Ni Laves phases and the closely related Haucke phases, $Ln_xLn'_{1-x}Ni_5$. Data are presented for eight ternary systems—four Haucke and four Laves phase systems.

II. Experimental Details

The procedures employed were essentially the same as those used in the earlier study (*1*). The nickel used was spectroscopic standard grade (99.999%) obtained from the Johnson-Matthey Co. Haucke phase systems form congruently from the melt. They were formed by fusing the components together and were used in the main without further heat treatment. A few alloys were annealed but experience showed that the magnetic behavior was unaffected by heat treatment. The Laves phases form peritectically and must be heat treated to secure a single phase material. They were sealed off under 100 mm of Ar and held at approx. 800C for upwards of a week. This treatment produced a single phase material as evidenced by their diffraction pattern.

Magnetic measurements were made as described earlier (*1*).

III. Results and Discussion

Results are largely summarized in Table I and in Figs. 1–8. As regards the Laves phase systems, the coupling pattern is seen to be in the main identical with that observed for the corresponding aluminum phases. Systems with only heavy lanthanides present are ferromagnetic whereas those containing Nd and Gd or Ho are ferrimagnetic. The moment of alloys

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TABLE I

MEASURED AND CALCULATED PARAMAGNETIC MOMENTS IN BOHR MAGNETONS PER Ln^{+3} ION

x	0	0.2	0.4	0.6	0.8	1.0
			$Gd_xDy_{1-x}Ni_2$			
(μ_{eff})meas	10.4	10.14	9.71	8.86	9.14	7.82
(μ_{eff})calc	10.60	10.12	9.63	9.10	8.54	7.94
			$Gd_xHo_{1-x}Ni_2$			
(μ_{eff})meas	10.5	10.2	9.58	8.95	8.51	7.82
(μ_{eff})calc	10.6	10.0	9.64	9.10	8.54	7.94
			$Gd_xNd_{1-x}Ni_2$			
(μ_{eff})meas	3.74	4.91	5.76	6.64	7.18	7.82
(μ_{eff})calc	3.62	4.84	5.77	6.58	7.29	7.94
			$Ho_xNd_{1-x}Ni_2$			
(μ_{eff})meas	3.74	5.67	7.35	8.58	9.45	10.5
(μ_{eff})calc	3.62	5.73	7.27	8.53	9.62	10.6
			$Gd_xDy_{1-x}Ni_5$			
(μ_{eff})meas	11.0	10.14	9.71	8.86	9.14	7.87
(μ_{eff})calc	10.6	10.12	9.63	9.10	8.54	7.94
			$Gd_xHo_{1-x}Ni_5$			
(μ_{eff})meas	10.5	10.1	9.72	8.99	8.38	7.87
(μ_{eff})calc	10.6	10.02	9.64	9.10	8.54	7.94
			$Gd_xNd_{1-x}Ni_5$			
(μ_{eff})meas	—[a]	—[a]	—[a]	—[a]	—[a]	7.87
(μ_{eff})calc	3.62	4.79	5.74	6.55	7.29	7.94
			$Ho_xNd_{1-x}Ni_5$			
(μ_{eff})meas	—[a]	6.11	7.56	8.72	9.84	10.5
(μ_{eff})calc	3.62	5.77	7.28	8.53	9.60	10.6

[a] Does not obey Curie-Weiss Law.

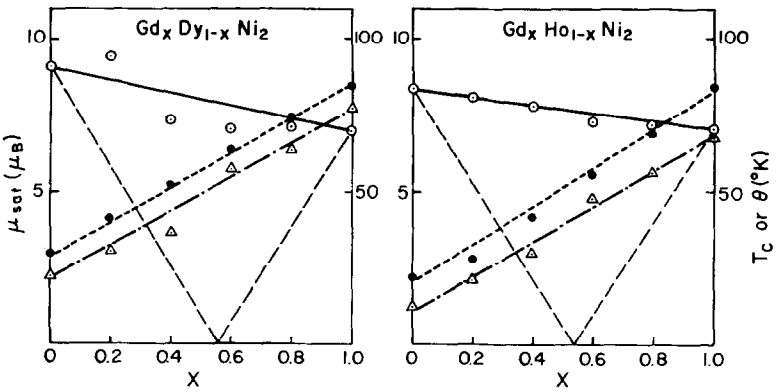

FIG. 1. Magnetic data for two Laves phase systems containing two heavy lanthanides combined with nickel. The variation of saturation moment (⊙), Weiss constant (△) and Curie temperature (●) with composition are shown. The full and dashed lines show the expected μ_{sat} values for ferromagnetic and antiferromagnetic coupling, respectively.

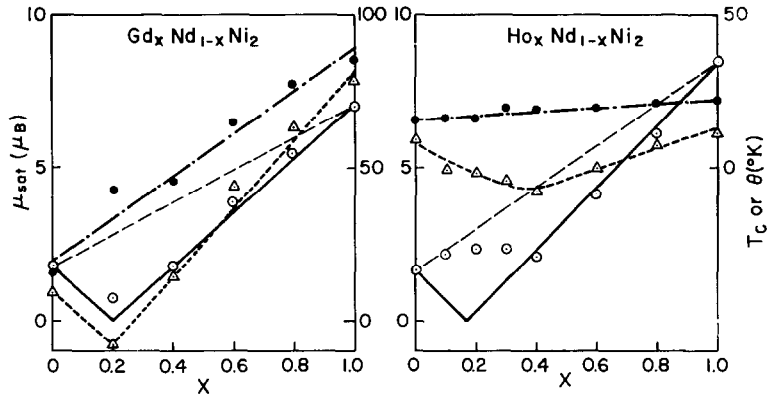

FIG. 2. Magnetic data for two Laves phase systems containing one heavy and one light lanthanide combined with nickel. The legend is the same as for Fig. 1 except that the full and dashed lines refer to antiferromagnetic and ferromagnetic coupling. respectively.

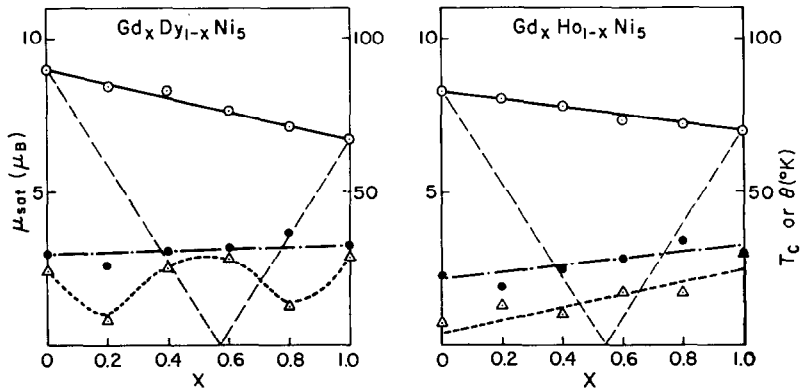

FIG. 3. Magnetic data for two Haucke phase systems containing two heavy lanthanides combined with nickel. The legend is the same as for Fig. 1.

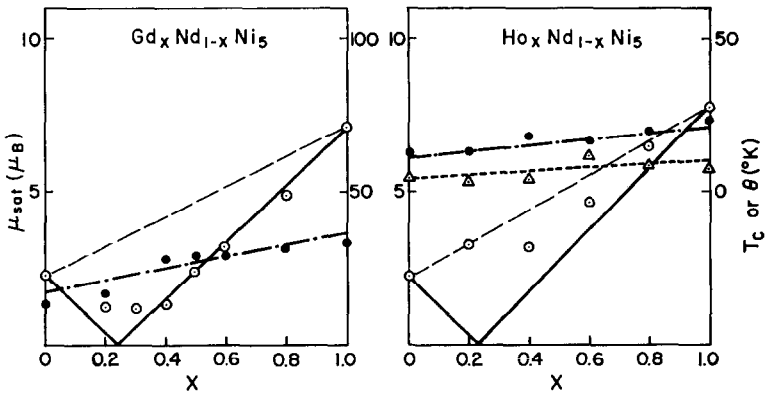

FIG. 4. Magnetic data for two Haucke phase systems containing one heavy and one light lanthanide combined with nickel. The legend is the same as for Fig. 2.

containing Dy shows considerable scatter about the straight line (Fig. 1) representing ferromagnetic coupling but the departures are insufficient to render the coupling pattern doubtful. The scatter is undoubtedly a crystal field effect—either directly by partially quenching the moment or indirectly

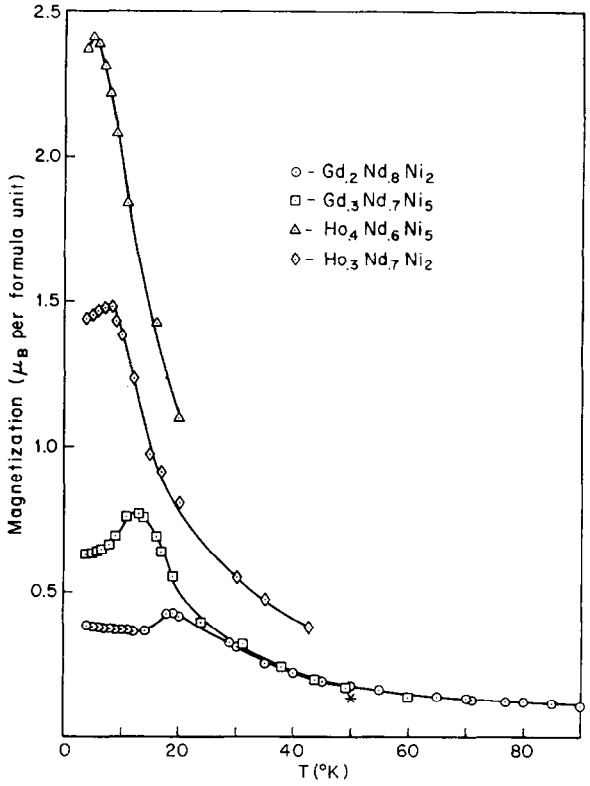

FIG. 5. Magnetization-temperature data for several Laves and Haucke phase ternary systems. The maximum suggests antiferromagnetic coupling of light and heavy lanthanides.

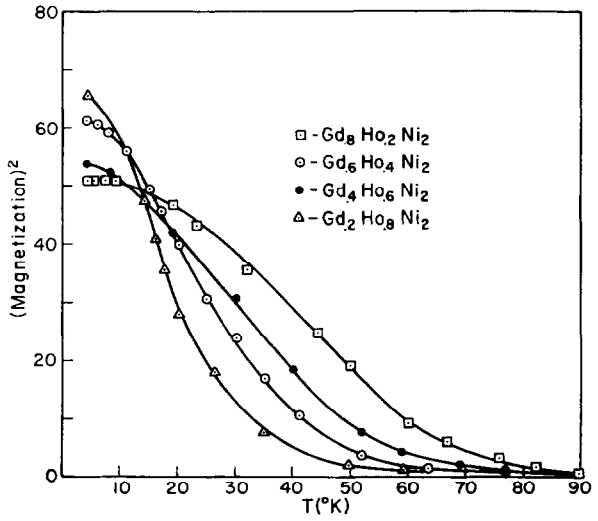

FIG. 6. A plot of the square of the magnetization (in μ_B formula unit) for typical ternaries containing two heavy lanthanides. The behavior is consistent with ferromagnetic coupling of the lanthanides in these ternaries.

through the anisotropy which makes it difficult to saturate these materials.

Antiferromagnetic coupling of Gd–Nd and Ho–Nd in the ternary Laves phases is evident not only from the composition dependence of the saturation magnetization (Fig. 2) but also from the variation

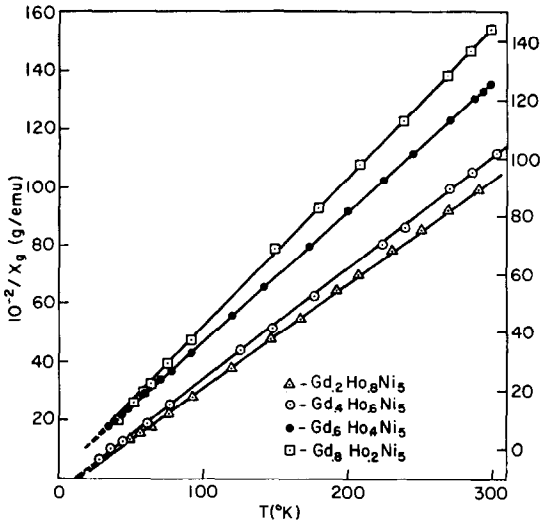

FIG. 7. Dependence of inverse susceptibility on temperature for $Gd_xHo_{1-x}Ni_5$ ternaries. These are typical of all the systems studied except the $Gd_xNd_{1-x}Ni_5$ ternaries.

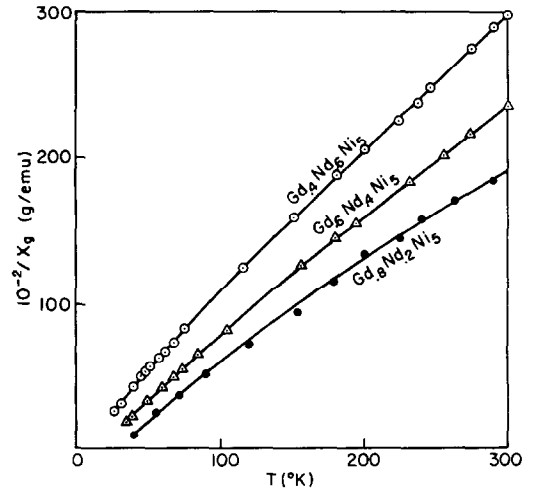

FIG. 8. Dependence of inverse susceptibility on temperature for $Gd_xNd_{1-x}Ni_5$ ternaries.

of the Weiss constant (θ) with composition and the dependence of magnetization on temperature (Fig. 5). θ passes through a minimum close to the point at which the moment is minimal, resembling the behavior noted for the ferrimagnetic systems $Dy_xPr_{1-x}Al_2$, $Ho_xPr_{1-x}Al_2$ and $Ho_xNd_{1-x}Al_2$ (*1*). In contrast with this θ varies linearly with composition for the ferromagnetic alloys and the magnetization-temperature is typical of that normally observed for ferromagnetic materials. The data shown in Fig. 6 for the $Gd_xHo_{1-x}Ni_2$ ternaries are representative of results obtained for all the ferromagnetic Laves and Haucke phases.

The observed moment in the Nd–Gd–Ni and Nd–Ho–Ni Laves phase ternaries deviates considerably from the value expected from antiferromagnetic coupling near the minimum in saturation moment. It appears that in these alloys the internal field is weakened to an extent that the applied field can induce ferromagnetic alignment of the two sublattices, enhancing the moment in this way.

In many respects the Haucke phase data closely resemble the results obtained for the Laves phases. Ferromagnetic coupling is indicated for the Gd–Dy–Ni and Gd–Ho–Ni ternaries. There is considerable scatter for the former system, again presumably due to the effect of the crystal field on the Dy moment. Results for the Gd–Nd–Ni Haucke phase ternaries clearly support the concept of antiferromagnetic coupling of the two lanthanides. Here also, as with the corresponding Laves phase systems, the moment is larger than expected (if the coupling is antiferromagnetic) near the minimum. Similar considerations undoubtedly apply.

Saturation magnetizations obtained for the $Ho_{1-x}Nd_xNi_5$ system are inconclusive as regards the coupling pattern (see Fig. 4). However, the magnetization of these alloys as well as the $Gd_{1-x}Nd_xNi_5$ alloys show (Fig. 5) an initial rise with increasing temperature followed by a maximum. This behavior suggests that Ho and Nd are antiferromagnetically coupled in the Ho–Nd–Ni ternaries.

Paramagnetic moments are listed in Table I together with the value expected from the effective moments of the lanthanide constituents. $\mu_{calc} = [x_1 g_1^2 J_1(J_1+1) + x_2 g_2^2 J_2(J_2+1)]^{1/2}$. Here x represents the atomic fraction of each constituent on the lanthanide sublattice and g and J have their usual significance. Neglecting the $Gd_{1-x}Nd_xNi_5$ system, the deviation between observed and calculated values is good. They deviate by only 1.8% on the average; this is within experimental error. Thus for seven systems the paramagnetic behavior is in keeping with expectation. Slight deviations from Curie–Weiss behavior in the region immediately above the ordering temperature are noted for some systems but this is not unanticipated. Representative plots of reciprocal susceptibility versus temperature are given in Fig. 7.

The dependence of reciprocal susceptibility on temperature for representative members of the $Gd_xNd_{1-x}Ni_5$ system is shown in Fig. 8. Pronounced deviations from linearity are noted and the Weiss constant rises to a large negative value for systems dilue in Nd. These effects, which are probably due to the interaction of the Nd^{+3} ion with the crystal

field, are absent in the $Ho_xNd_{1-x}Ni_5$ system. This suggests that the crystal field interaction is weaker in the Ho-containing ternaries. Superficially this difference seems surprising. However, in studies of Al-containing intermetallics it has become evident (*3*, *4*) that the conduction electrons are significantly involved in determining the sign and magnitude of the crystal field. Their contribution is in turn dependent on the band structure, and more particularly the spatial location of the conduction electrons, of the system involved. The difference in behavior of the $Ln_xNd_{1-x}Ni_5$ systems with Ln = Gd and Ho implies a significant difference in these features for the two systems.

In terms of regularity of variation of T_c, θ and μ_{sat} on composition the Haucke phases are as a class less ideal than the Laves phases. This feature merits comment. In the Al-containing Laves phase ternaries the magnetic interactions involve the lanthanides exclusively. In the nickel-containing Laves phase Haucke phase ternaries, nickel is nonmagnetic (*5*); it is presumed (*5*) to be in a $3d^{10}$ configuration as a result of electron transfer from the lanthanide with which it is in chemical union. Since excitation of the nickel into a magnetic state is probably not too difficult energetically, nickel could be involved to some extent in the magnetic interactions. This is particularly the case for the Haucke phases in which electron transfer is rather extensive to render all nickels nonmagnetic. Involvement of nickel in the magnetic interaction would probably make the $Ln_xLn'_{1-x}Ni_2$ systems behave differently than their Al counterparts. The regularity of behavior of the Ni Laves phases indicates that nickel is not significantly involved in the interactions, whereas in the Haucke phases it is involved to some extent either directly, as suggested above, or indirectly by depleting the electron concentration of the system. The Haucke phases seem to represent an intermediate situation between the $LnNi_2$ (or $Ln_xLn'_{1-x}Ni_2$) systems on the one hand and the $LnCo_2$ systems on the other. The latter are magnetically more complex than the corresponding Nickel systems (*5*) presumably because of difficulty in filling the Co 3*d* band.

References

1. W. M. Swift and W. E. Wallace, *J. Phys. Chem. Solids* **29**, 2053 (1968).
2. H. J. Williams, J. H. Wernick, R. C. Sherwood, and E. A. Nesbitt, *J. Phys. Soc. Japan* **17**, Suppl. B-I, 91 (1961).
3. K. H. Mader, E. Segal, and W. E. Wallace, *J. Phys. Chem. Solids* **30**, 1 (1969).
4. J. A. White, H. J. Williams, J. H. Wernick, and R. Sherwood, *Phys. Rev.* **131**, 1039 (1963).
5. John Farrell and W. E. Wallace, *Inorg. Chem.* **5**, 105 (1966).