Magnetic Characteristics of LnCo₅-ThCo₅ Pseudobinary Systems*

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Magnetic characteristics of $Ln_{1-x}Th_xCo_5$ ternaries, with Ln = Gd, Ho or Er, are reported. This introduced into the lattice in an effort to achieve ferromagnetic coupling. It is observed that the antiferromagnetic Ln-Co coupling, which exists in the LnCo₅ binaries, also persists in the ternaries. The cobalt moment and Curie temperature are reduced as the Th content of the sample is increased. The decreased cobalt moment is ascribed to electron transfer from Th to the cobalt *d*-shell. Failure to achieve ferromagnetism in the ternaries is ascribed to electron capture by cobalt, which prevents a rise in electron concentration as Th replaces Ln in the lattice.

I. Introduction

This investigation forms part of a continuing series of investigations being carried out in this laboratory (1, 2) in attempts to produce erromagnetic Ln–Co coupling in heavy lanthanide LnCo₅ systems. These efforts were initiated with the work of Shidlovsky and Wallace (1) on GdCo₅-based ternaries.

LnCo₅ systems, with Ln = Sm, Ce, Pr and Y, are of considerable significance as permanent magnet materials (3). The corresponding systems with the heavy rare earths (Gd, Dy, etc.) are potentially even more useful because of the large rare earth contribution. Actually they have not proved to be of interest to date in connection with permanent magnet technology because the Ln and Co sublattices are antiferromagnetically coupled. A series of studies is under way in this laboratory to ascertain whether the coupling can be reversed by alloying so as to modify the electron concentration. Reversal of coupling is expected if the Ln–Co moments interact via the RKKY mechanism (4).

In the earlier work (1) modification of the LnCo₅ coupling was attempted by substitution on the cobalt sublattice with Al and Cu. The

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Copyright © 1973 by Academic Press, Inc. All rights of reproduction in any form reserved. Printed in Great Britain present work involves substitution on the Ln sublattice; trivalent Gd, Ho and Er are replaced by quadrivalent Th with the intention of increasing the electron concentration and reversing the Ln-Co coupling.

II. Experimental Details

The ternaries were prepared, using the best grades of metals available commercially, by induction heating under purified argon in a water cooled copper boat. Stoichiometric HoCo₅ and ErCo₅ actually consisted of two phases (LnCo₅ and Ln₂Co₇). For these systems single phase materials occur only at compositions $HoCo_{5.5}$ and $ErCo_6$. This deviation from ideal LnCo₅ stoichiometry is also true for ternary phases containing Ho and Th or Er and Th that are relatively dilute in Th. As the Th content increases, the stoichiometry of the single phase material becomes ideal. The stoichiometries of the ternaries studied, all of which were single phase, are given in Table I. Magnetic measurements were made using equipment and techniques which are now standard in this laboratory (5).

III. Result and Discussion

Saturation magnetizations, measured at 4.2 K, and Curie temperatures are listed in Table I. In

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TABLE I

	$\mu_{\rm sat}(\mu_{\rm B/f.u.})$	μ _{Co(cale)}	<i>T</i> _c (K)
GdCo₅	1.50	1.70	1030ª
Gd.8Th.2Cos	2.57	1.63	980
Gd.6Th.4Co5	2.99	1.44	873
Gd_4Th_6Co5	3.89	1.34	772
Gd_2Th_4Cos	4.22	1.12	663
HoCo _{5.5}	1.38	1.57	~1066
Ho.8Th.2Co5.5	1.41	1.71	>1000
Ho. ₆ Th.₄Co₅	2.63	1.72	831
Ho,4Th,6Co5	4.35	1.67	754
Ho ₂ Th ₈ Co ₅	5.28	1.46	680
ErCo ₆	1.25	1.71	~1123
Er.8Th.2Co5.5	2.47	1.61	>1000
Er_6Th_4Co5.5	3.33	1.59	~1000
Er_4Th_6Co5	3.55	1.43	762
Er_2Th_8Co5	4.56	1.27	652
ThCo ₅	4.62	0.92	550

^a From Ref. (6).

general, the magnetic behavior of the $Ln_{1-x}Th_x$ -Co₅ ternaries is very similar to that exhibited by the GdCo_{5-x}Al_x and GdCo_{5-x}Cu_x ternaries studied earlier (1). There are two aspects of the similarity that merit comment. First, the magnitude of the measured moments clearly indicates that the antiferromagnetic Ln-Co coupling is not modified when Th is introduced into the lattice. Second, the cobalt moment is reduced as the ternary is formed. The cobalt moment (column 3 of Table I) has been computed from the saturation magnetizations under the following assumptions: (a) the Ln-Co coupling is antiferromagnetic, (b) Th is nonmagnetic and (c) Gd, Ho and Er have moments of 7.0, 10.0 and 9.0 $\mu_{\rm B}$, respectively. The reduction in $\mu_{\rm Co}$ as Th is introduced into the lattice implies absorption by cobalt into its *d*-shell or *d*-band of the extra electrons brought in by Th. Thus, efforts to increase the electron concentration may have been unsuccessful. It is perhaps for this reason that alloying failed to produce the desired reversal of Ln-Co coupling.

 μ_{Co} in the HoCo_{5.5} system appears to rise as Ho is replaced by Th. It passes through a shallow maximum at x = 0.4. This rise may merely be a consequence of the assumptions involved in computing μ_{Co} , specifically that μ_{Ho} is constant at 10 μ_{B} per atom.

We note that the Curie temperature is reduced as μ_{Co} decreases.

References

- I. I. SHIDLOVSKY AND W. W. WALLACE, J. Solid State Chem. 2, 193 (1970).
- H. J. SCHALLER, R. S. CRAIG, AND W. E. WALLACE, J. Appl. Phys. 43, 3161 (1972).
- 3. J. J. BECKER, J. Appl. Phys. 41, 1055 (1970).
- 4. For a discussion of the RKKY interaction and reversal of coupling see W. E. WALLACE, "Rare Earth Intermetallics," Chapt. 2 and 10, Academic Press, New York, 1973.
- R. A. BUTERA, R. S. CRAIG, AND L. V. CHERRY, *Rev. Sci. Instr.* 32, 708 (1961).
- 6. W. E. WALLACE, Progr. Solid State Chem. 6, 155 (1971).