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Magnetic Properties of $Gd_{1-x}Th_xFe_2$ and $Gd_{1-x}Ce_xFe_2$*

E. T. MISKINIS, K. S. V. L. NARASIMHAN, W. E. WALLACE, AND R. S. CRAIG

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

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Saturation magnetization, magnetization vs temperature, Curie temperatures, and lattice parameters are presented for the ternary alloys $Gd_{1-x}Th_xFe_2$ and $Gd_{1-x}Ce_xFe_2$. Quadrivalent Th and Ce were introduced into the lattice in an effort to induce ferromagnetic Gd–Fe coupling. Experiment showed that the antiferromagnetic Gd–Fe coupling in $GdFe_2$ is preserved in the ternaries. The Fe moment and Curie temperature decrease as the Gd content of the sample is decreased. This is ascribed to electron transfer from Th or Ce to the Fe *d* shell. Failure to achieve ferromagnetic coupling is ascribed to electron capture by iron, which prevents a rise in electron concentration as Gd is replaced by Ce or Th.

I. Introduction

This investigation and the following study form part of a continuing series of investigations being carried out in this laboratory (*1*, *2*) in attempts to produce ferromagnetic Ln-transition metal coupling in heavy lanthanide Ln–Co or Ln–Fe systems. These efforts were initiated with the work of Shidlovsky and Wallace (*1*) on $GdCo_5$-based ternaries.

$LnCo_5$ 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 useful 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 in these and in Ln–Fe systems by alloying so as to modify the electron concentration. Reversal of coupling is expected if the Ln-transition metal moments interact via the RKKY mechanism (*4*).

In the earlier work (*1*) modification of the $LnCo_5$ coupling was attempted by substitution on the cobalt sublattice with Al and Cu. The present work involves substitution on the lanthanide sublattice; trivalent Gd in $GdFe_2$ is replaced by quadrivalent Th with the intention of increasing the electron concentration and thereby reversing the Ln–Fe coupling. This study is very similar in concept to the recent study of Wallace and Swearingen (*5*), except that in the previous work the hexagonal 1:5 cobalt compound was used, whereas the present study deals with a cubic 1:2 iron compound. In addition to the study of ternaries containing Th, the system $Gd_{1-x}Ce_xFe_2$ was examined since Ce in these alloys seems to behave quadrivalently (*6*).

II. Experimental Details

The materials used to make the rare-earth transition metal ternaries have the following reported purity, exclusive of gaseous contaminants: Gd: 99.9% by weight; Ce: 99.9% by weight; Th: 99.99% by weight. The Fe was Johnson–Matthey spectroscopic standard grade with impurities less than 50 ppm. The alloys were prepared by induction melting in a water-cooled copper boat under a flowing

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atmosphere of purified argon gas. The weight losses were of the order of 0.05% or less. The ingots were subsequently wrapped in tantalum foil and annealed in vacuum at 800°C for two weeks. All the compounds were examined by X-ray and thermomagnetic analysis for single-phase homogeneity. Lattice constants were obtained by a linear least-squares iterative fit of the observed 2θ values. The error in the lattice parameter is estimated to be ± 0.002 Å. All the compounds were found to crystallize in the cubic $MgCu_2$ type structure.

Magnetic measurements were made using the Faraday method in fields up to 20 kOe employing loosely packed powders. The equipment used and technique employed are now standard in this laboratory (*7*). Saturation moments were obtained from magnetization vs inverse field plots by extrapolating to $1/H = 0$. Curie temperatures were obtained from plots of magnetization squared vs temperature extrapolating to zero magnetization.

III. Results and Discussion

Experimental results are largely summarized in Tables I and II and in Figs. 1–3. The retention of antiferromagnetic coupling between Gd and Fe for the ternary systems is evident from the tabulated results. For example, with $Gd_{0.6}Ce_{0.4}Fe_2$ the moment expected, if Gd and Fe were coupled ferromagnetically and the individual moments were the same as those

TABLE I

MAGNETIC AND STRUCTURAL PROPERTIES OF $Gd_{1-x}Ce_xFe_2$ COMPOUNDS

x	a (Å)	μ_{sat} (μ_B/f.u.)	Iron moment assuming Ce^{4+} (μ_B/Fe atom)	T_c (°K)
0	7.362	3.58	1.71	810
0.2	7.374	2.32	1.64	740
0.4	7.352	1.08	1.56	650
0.6	7.334	0.56	1.18	560
0.8	7.302	1.49	1.45	430
1.0	7.288	2.38	1.19	240

TABLE II

MAGNETIC AND STRUCTURAL PROPERTIES OF $Gd_{1-x}Th_xFe_2$ COMPOUNDS

x	a (Å)	μ_{sat} (μ_B/f.u.)	Iron moment (μ_B/Fe atom)	T_c (°K)
0.12	7.412	3.12	1.52	760
0.29	7.431	1.13	1.92	700
0.42	7.442	0.40	1.83	620
0.51	7.468	0.17	1.72	610
0.71	7.510	0.97	1.50	490

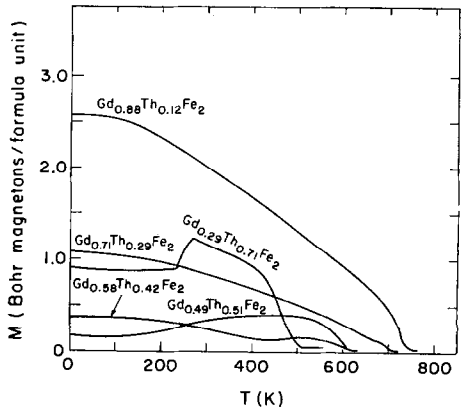

FIG. 1. Variation of magnetization as a function of temperature in an applied field of 6 kOe for Gd–Th–Fe ternaries.

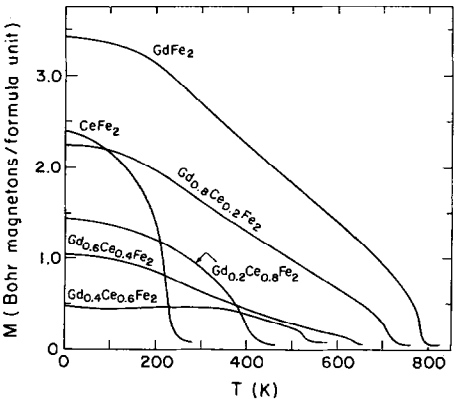

FIG. 2. Variation of magnetization as a function of temperature in an applied field of 6 kOe for Gd–Ce–Fe ternaries.

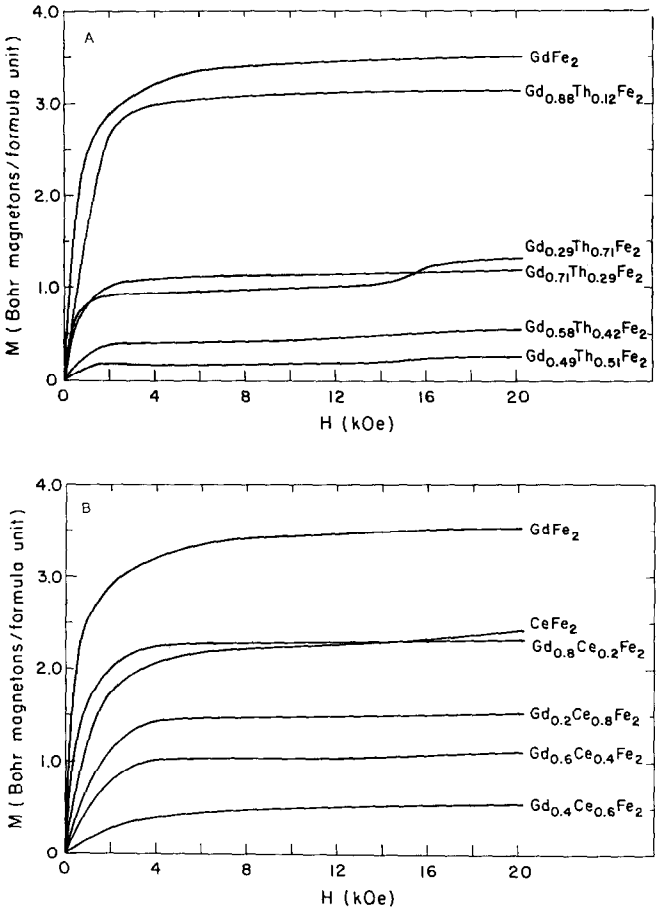

FIG. 3. (A) Variation of magnetization as a function of field in $Gd_{1-x}Th_xFe_2$. The rise in magnetization at about 16 kOe for $Gd_{0.29}Th_{0.71}Fe_2$ is consistent with the inference that this alloy contains a small amount of $ThFe_3$ impurity (see text and Refs.(*8*) and (*9*)). (B) Variation of magnetization as a function of field in $Gd_{1-x}Ce_xFe_2$

in $GdFe_2$, i.e., 7 and 1.71 μ_B, respectively, is 7.62 μ_B/formula unit (f.u.). This contrasts sharply with the experimental value of 1.08 μ_B/f.u. Examination of all the ternaries studied leads to a similar conclusion—the inclusion of Th or Ce in the lattice does not alter the nature of the Gd–Fe coupling.

From Fig. 3 it is clear that the alloys saturate readily at 4.2 K since an applied field of 20 kOe is adequate for saturation. These materials are magnetically soft. The non-Brillouin shape of the magnetization–temperature behavior for $GdFe_2$ is also evident for ternaries in which only a small fraction of Gd has been replaced by Ce or Th (Figs. 1 and 2). The shape of these curves renders the determination of T_c somewhat inaccurate so the values of T_c listed in Tables I and II are probably not reliable to better than 10 K.

For the $Gd_{0.29}Th_{0.71}Fe_2$ ternary there is a sharp rise in magnetization with increasing temperature between 200 and 300 K. This alloy is at the limit of stability of the cubic structure as evidenced by X-ray investigations and it appears that a small amount of $ThFe_3$ may exist in the sample. ($ThFe_2$ does not form.) This surmise is a consequence of work by Kunesh et al. who have shown that $ThFe_3$ and the substituted ternaries (*8*, *9*) exhibit a sharp rise in their magnetization–temperature curves between 200 and 250 K.

If one assumes antiferromagnetic Gd–Fe

coupling, nonmagnetic Ce (i.e., Ce^{4+}) and a Gd moment constant at 7 μ_B, one obtains Fe moments as shown in column 4 of Tables I and II. Although the details of these results, particularly those for the Th ternary, do not lend themselves to any simple interpretation there is an unmistakable trend of a reduction in Fe moment when the concentration of Th or Ce in the lattice is increased. The Fe moment falls from 1.71 μ_B for $GdFe_2$ to 1.19 μ_B for $CeFe_2$, and to 1.50 μ_B for the Th ternary at the phase boundary. This decrease is ascribed to increased filling of the *d*-band or *d*-shell when trivalent Gd is replaced by quadrivalent Th. Behavior when Gd is replaced by Ce is similar. The rise in iron moment for small Th substitutions is probably due to the fact that vacancies exist in both the spin up and spin down bands (or shells); these are filled at different rates, giving rise to the increased net moments shown. However, these details cannot be fully clarified in the absence of specific information about the electronic configuration of Fe in these materials.

If electrons are indeed absorbed by Fe, efforts to increase the electron concentration by forming the Th or Ce alloys may have been unsuccessful. This may underlie the failure to achieve ferromagnetic coupling in the several ternaries studied in this work.

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