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Magnetic and Structural Studies of Rare Earth–Iron–Manganese Laves Phase Ternaries II

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Structures, magnetic properties and Mössbauer spectra of the systems $Gd(Fe_{1-x}Mn_x)_2$, $Tb(Fe_{1-x}Mn_x)_2$, and $Dy(Fe_{1-x}Mn_x)_2$ are presented. The Tb and Dy alloys possess the $C15$ structure for all values of x. The Gd alloys possess the $C15$ structure for x ranging from 0 to 0.2 and from 0.8 to 1.0; an intermediate phase of different, and as yet unknown, structure exists in the range $x = 0.5$ to 0.6. The Curie temperature and the Fe hyperfine field are reduced as Mn replaces Fe in the lattice. These effects are taken to be a consequence of antiferromagnetic Fe–Mn interactions.

I. Introduction

A series of investigations is under way in this laboratory dealing with the structural and magnetic characteristics of ternary intermetallics containing iron and manganese. The principal objective is to determine whether the insertion of Mn into a binary system in which one component is Fe results in an enhancement or reduction of ferromagnetic exchange. In an earlier paper (hereafter referred to as I) results were presented (*1*) for $Er(Fe_{1-x}Mn_x)_2$ and $Ho(Fe_{1-x}Mn_x)_2$. The present paper deals with the corresponding Gd, Tb, and Dy ternaries. In I it was not possible to have continuous miscibility of the Fe and Mn compounds since the former exist in the cubic $C15$ structure where as $HoMn_2$ and $ErMn_2$ occur in the hexagonal $C14$ structure. In contrast, complete miscibility is possible for the Gd, Tb, and Dy ternaries since all six terminal phases exist in the cubic $C15$ structure.

The present study was undertaken to determine the phase relations in the RMn_2–RFe_2 pseudobinary systems, with $R = Gd$, Tb, and Dy, and to determine the effect of composition on the magnetic properties of the ternaries. Since we are interested in systems suitable for use in devices we have confined attention to room temperature and above.

The experimental procedures employed are the same as those described in I.

II. Results and Discussion

Diffraction results showed immediately that RFe_2 and RMn_2, where R is Tb or Dy, are miscible in all proportions. Surprisingly, the Gd ternaries behave differently. There are terminal phases based on $GdFe_2$ and $GdMn_2$ and an intermediate phase having a different structure, extending over the range $Gd(Fe_{0.5}Mn_{0.5})_2$ to $Gd(Fe_{0.3}Mn_{0.7})_2$. Schematic diffraction patterns for $GdFe_2$, $Gd(Fe_{0.6}Mn_{0.4})_2$ and $Gd(Fe_{0.4}Mn_{0.6})_2$ are shown in Fig. 1. On the basis of the Mössbauer spectra (vide infra) we regard the latter as essentially single phase and having an as yet unsolved structure, which we designate as the "x" structure. $Gd(Fe_{0.6}Mn_{0.4})_2$ is a two phase mixture of the $C15$ terminal phase based on $GdFe_2$ and the "x" structure. Phase relations for the five $R(Fe_{1-x}Mn_x)_2$ systems that have been studied are shown in Fig. 2. Lattice constants, plotted in Fig. 3, show negative deviations from the behavior expected from Vegard's Law.

Representative magnetization-temperature behavior for the systems is shown in Figs. 4

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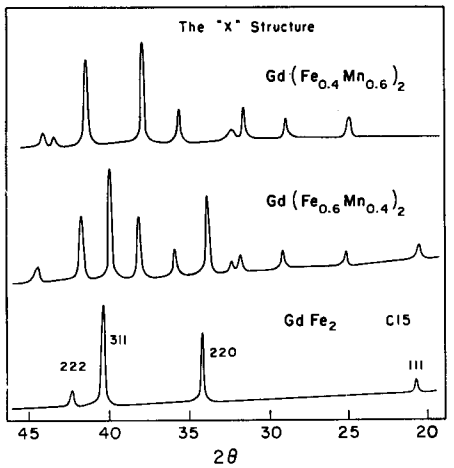

FIG. 1. Schematic diffraction patterns of $GdFe_2$, $Gd(Fe_{0.6}Mn_{0.4})_2$, and $Gd(Fe_{0.4}Mn_{0.6})_2$. Results for the latter ternary indicate that it does not have the $C15$ structure possessed by the parent binary compound. Its structure is designated "x". $Gd(Fe_{0.6}Mn_{0.4})_2$ is a mixture of phases having the $C15$ and "x" structure.

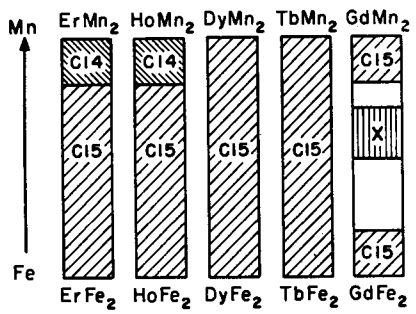

FIG. 2. Phase relationships for $R(Fe_{1-x}Mn_x)_2$ systems. The region marked x involves an unknown structure. The blank spaces represent two phase regions involving the $C15$ and x structures.

and 5. The decline in ordering temperature (T_c) as Fe is replaced by Mn is readily apparent. In this respect the present systems behave similarly to the two systems described in I, the Y_6Fe_{23}–Y_6Mn_{32} pseudobinaries (*2*) and the $Fe_{3-x}Mn_xSn$ (*3*) and $Fe_{3-x}Mn_xGe$ (*4*) systems. As pointed out in I the Fe–Mn distances are in the range in which antiferromagnetic Fe–Mn coupling is anticipated. Therefore, we ascribe the reduction in T_c to the increasing importance of antiferromagnetic exchange as the Mn concentration is increased.

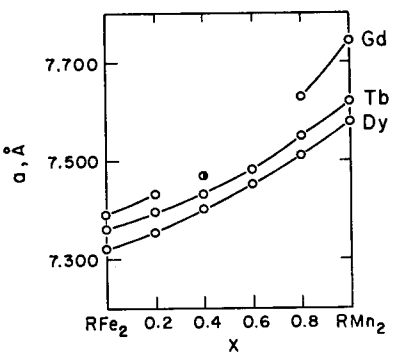

FIG. 3. Lattice constants at room temperature for $R(Fe_{1-x}Mn_x)_2$ systems.

The $DyFe_2$ Fe^{57} Mössbauer spectrum obtained at room temperature is a normal six-line pattern very similar to that obtained by Bowden et al.[5] Incorporation of 10% Mn in place of Fe in the lattice gives rise to a complex spectrum, containing more than one six-line pattern. This is undoubtedly due to a variety of internal fields at the Fe^{57} nucleus. The only certain feature is that the hyperfine field in $DyFe_2$ has been reduced significantly when Fe is replaced by Mn. The Fe^{57} Mössbauer spectrum for $TbFe_2$ is also similar to that obtained by Bowden et al (*5*) and indicates two hyperfine fields, which is expected since for this material the easy axis of magnetization is in the 111 direction. Incorporation of Mn in the Fe sublattice leads to spectra qualitatively similar to those obtained for $Dy(Fe, Mn)_2$ ternaries.

In general, the Mössbauer spectra are similar for the three systems in the present work and the two systems in I, except for the region in the Gd ternaries in which the system exists in the "x" structure. Data for $Gd(Fe_{0.4}Mn_{0.6})_2$, which has the "x" structure, are shown in Fig. 6. The spectrum for this material appears to consist of a singlet. There is an indication of a shoulder, suggesting that a small amount of the $C15$ structure may be present along with the "x" structure. The simplicity of the Mössbauer spectrum for this material provides strong suggestive evidence to indicate that the region ascribed to the "x" structure does indeed correspond to a single phase material.

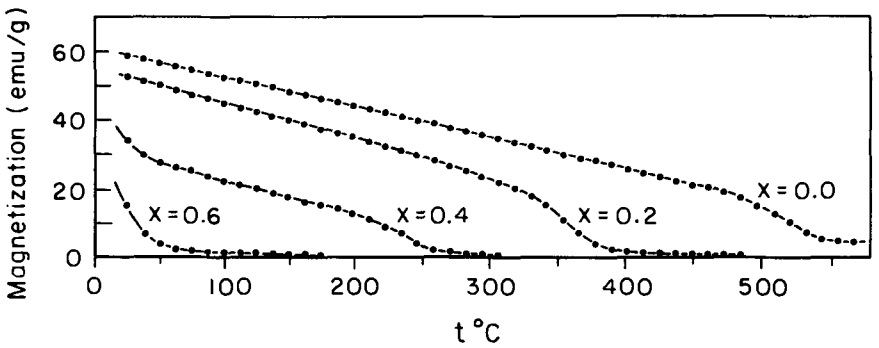

FIG. 4. Magnetization-temperature curves for $Gd(Fe_{1-x}Mn_x)_2$ ternaries.

In the ferromagnetic region the Mössbauer spectra for the $R(Fe, Mn)_2$ ternaries are too complex for a proper analysis to be made. As noted above, this is undoubtedly due to the existence of a range of hyperfine fields in the material occasioned by the random distribution of Fe and Mn over the transition metal sublattice. When the Mn content is increased to the point that magnetic ordering occurs only below room temperature, the Mössbauer pattern measured at room temperature is very much simplified and is susceptible to analysis. It consists of a doublet (Fig. 7), presumably a consequence of the quadrupole interaction. The quadrupole interactions observed for the several $R(Me, Fn)_2$ ternaries are given in Table I. The results indicate a systematic variation in the electric field gradient with the atomic number of R and with the Fe content of the system. Raising the Fe content or lowering the atomic number of R increases the

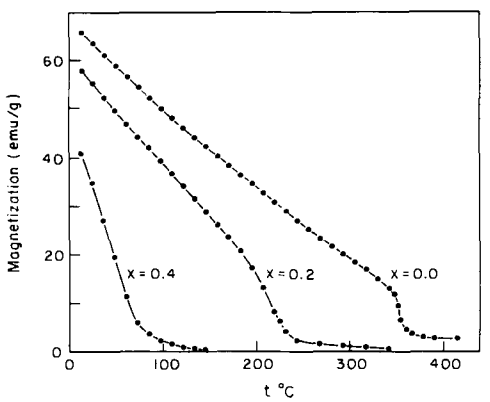

FIG. 5. Magnetization-temperature curves for $Dy(Fe_{1-x}Mn_x)_2$ ternaries.

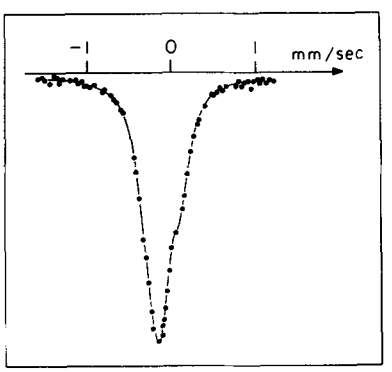

FIG. 6. Mössbauer spectrum for the intermediate phase $GdFe_{0.8}Mn_{1.2}$.

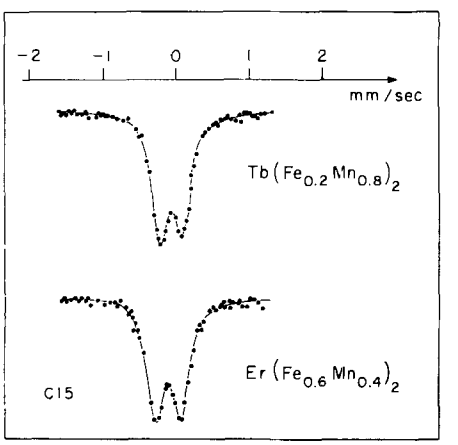

FIG. 7. Representative room temperature Mössbauer spectra of the $R(Fe, Mn)_2$ ternaries which show a doublet. These systems are in the paramagnetic range and the doublet is due to the quadrupole interaction. Both ternaries have the cubic $C15$ structure.

TABLE I

QUADRUPOLE SPLITTING (mm/sec) AT ROOM TEMPERATURE

	$R(Fe_{0.2}Mn_{0.8})_2$		
Gd	0.29		
Tb	0.24		
Ho	0.19		
Er	0.19		
	$R(Fa_{1-x}Mn_x)_2$		
	$x = 0.4$	0.6	0.8
Tb		0.37	0.24
Ho	0.33	0.29	0.19
Er	0.33	0.29	0.19

electric field gradient. The former results in a decrease of lattice parameter whereas the latter expands the lattice. Consequently the enlarged electric field gradient is not a simple consequence of the shrinkage of the lattice.

Acknowledgment

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