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

A. S. ILYUSHIN* AND W. E. WALLACE

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

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Structures, magnetic properties, and Mössbauer spectra of the systems $Er(Fe_{1-x}Mn_x)_2$ and $Ho(Fe_{1-x}Mn_x)_2$ are presented. The alloys are $C15$ structure for x in the range 0 to 0.6 and $C14$ for higher values of x. Incorporation of Mn in the lattice decreases the Curie temperature (T_c), presumably due to antiferromagnetic Fe–Mn interactions. For $x > 0.2$ the Mössbauer spectra at 300°K is a doublet since $T_c < 300°K$; the doublet splitting decreases with increasing x. Analysis of the structural results indicates that the charge on the Mn cores is higher in the $C14$ than in the $C15$ structure alloys.

I. Introduction

The compounds represented by the formula RFe_2, where R is a rare earth (except Pr or Nd) or yttrium, form in the cubic Laves phase ($C15$) structure. These materials have been extensively studied, particularly their magnetic properties (*1*). YFe_2 (*2*), $CeFe_2$, and $SmFe_2$ are ferromagnets with Curie temperatures (T_c) of 550, 235, and 700°K, respectively. The other RFe_2 materials have T_c in the range ~600–800°K and are ferromagnetically coupled; there is ferromagnetic coupling on the R and Fe sublattices, and the R and Fe sublattices are coupled antiferromagnetically.

We have undertaken a series of studies in this laboratory dealing with ternary systems of the formula $R(T_{1-x}T'_x)_2$, where T and T' represent two transition metals. Studies are being made of systems in which $T =$ Fe and $T' =$ Mn or Co. The present study, dealing with $R(Fe_{1-x}Mn_x)_2$, with $R =$ Ho and Er is the first completed work. These systems attracted our attention for several reasons: (a) $ErFe_2$ is congruent melting, and hence, ternaries based on it represent a simple preparation problem. (b) $ErMn_2$ and $HoMn_2$ occur in the $C14$ hexagonal Laves phase structure whereas $ErFe_2$ and $HoFe_2$ are cubic $C15$. The ranges of stability of the $C14$ and $C15$ structures in the ternary systems are of obvious interest. (c) The Fe–Mn coupling is antiferromagnetic in other pseudobinary systems, e.g., Y_6Fe_{23}–Y_6Mn_{23}, Fe_3Ge–Mn_3Ge, Fe_3Al–Mn_3Al, etc. (*3–5*). It is of interest to ascertain whether or not this is also true for the present systems. Additionally, it was hoped that the present work would shed light on the factors responsible for the structural differences between the RFe_2 and RMn_2 compounds. In regard to the latter it is to be noted that in the RMn_2 series we observe the $C15$ structure for $R =$ Gd, Tb, and Dy and the $C14$ structure for $R =$ Er and Tm, $HoMn_2$ is dimorphic, occurring in either the $C15$ or $C14$ structures, depending on its thermal history. The reasons why $HoMn_2$, $ErMn_2$, and $TmMn_2$ occur in the $C14$ structure have never been entirely clear. It was hoped that the present work might clarify this issue.

II. Experimental

Samples were prepared by induction melting of the component metals in a water-cooled copper boat. While molten, they were in an atmosphere of purified Ar. The best grade

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* Visiting scholar from the Department of Physics, Moscow State University, U.S.S.R.

metals available were used, 99.9% pure or better with respect to metallic impurities. Compositions were prepared and investigated with x increasing from 0 to 1 in steps of 0.2; $Er(Fe_{0.1}Mn_{0.9})_2$ was also studied.

X-ray diffraction information was obtained using a Picker unit equipped with a Cu tube. Magnetization was measured by the Faraday method. ^{57}Fe Mössbauer spectra were obtained using an Elron unit.

III. Results and Discussion

For both ternaries the diffraction measurements indicated the occurrence of the *C*15 structure from $x = 0$ to $x = 0.6$. The *C*14 structure is observed from $x = 0.8$ to 1.0. Sketches of the diffractometer traces for the $Er(Fe_{1-x}Mn_x)_2$ system for $x = 0.6$, 0.8, 0.9, and 1.0 are given in Fig. 1. These are typical for the two systems. The broadness of the 103 reflection for $x = 0.8$, which is near the *C*14 phase limit, is ascribed to stacking faults. These are presumably the precursors to the formation of the *C*15 structure at lower Mn concentrations. The 213 and 205 lines are also broadened for $x = 0.8$.

Magnetization versus temperature behavior of $ErFe_2$ and $Er(Fe_{0.8}Mn_{0.2})_2$ is shown in Fig. 2. Corresponding data for the Ho ternaries are shown in Fig. 3. The reduction in T_c by Mn is clearly evident. In this respect, the present systems behave similarly to the several Fe–Mn ternary systems mentioned in the Introduction. We take the reduced ordering temperature to be a consequence of antiferromagnetic exchange between Fe and Mn, the distance being such that this is expected. This follows inasmuch as systematic studies of Mn alloys have shown that Mn experiences antiferromagnetic exchange with itself (*6*)

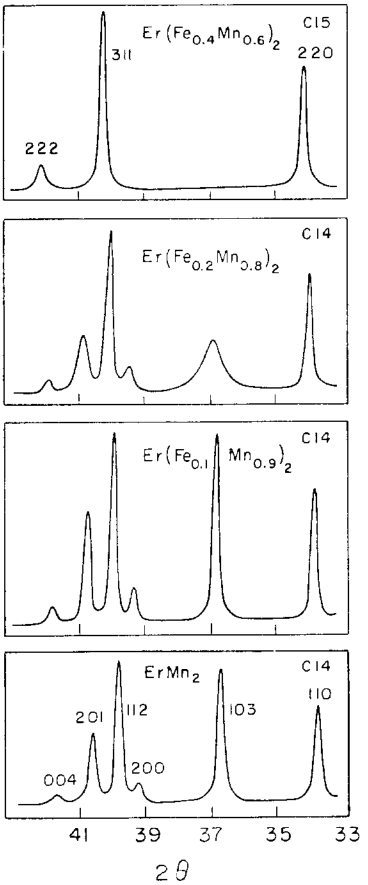

FIG. 1. Schematic representation of the diffraction pattern for $ErMn_2$ and several $Er(Fe,Mn)_2$ ternaries.

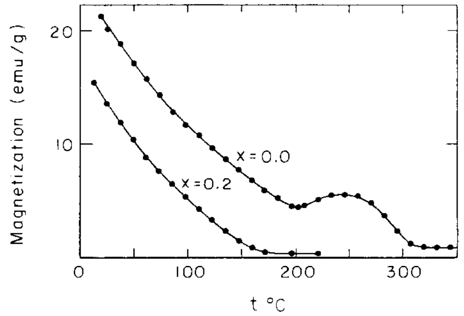

FIG. 2. Magnetization versus temperature for $ErFe_2$ and $Er(Fe_{0.8}Mn_{0.2})_2$.

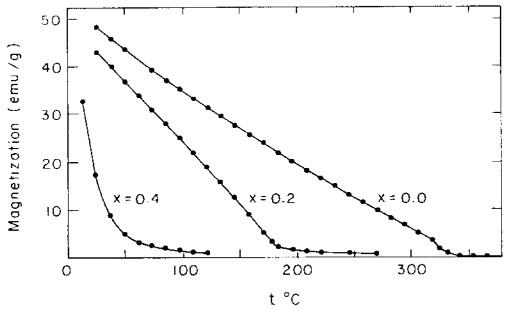

FIG. 3. Magnetization versus temperature for $HoFe_2$ and two $Ho(Fe,Mn)_2$ ternaries.

and with other 3*d* transition metals if the separation distance is less than about 2.8Å. The Mn–Mn or Mn–Fe distances in the present *R*–Mn–Fe ternaries is 2.6Å or less.

^{57}Fe Mössbauer spectra were obtained for the two series at 25°C. In agreement with the results of Bowden *et al.* (*7*), the data indicate two Fe hyperfine fields for $ErFe_2$ and one hyperfine field for $HoFe_2$. This is in accord with ⟨111⟩ and ⟨100⟩ anisotropies for $ErFe_2$ and $HoFe_2$, respectively. When x is increased from 0 to 0.2, the Mössbauer pattern becomes uninterpretable, except that it indicates (1) that the system is magnetically ordered and (2) the field at the Fe site has been reduced by about 10%. The complex spectrum is undoubtedly due to a distribution of hyperfine fields produced by the random distribution of Fe and Mn over the sublattice sites. When x is increased to 0.4, the Mössbauer pattern in a doublet, indicating that $T_c < 25°C$. The doublet splitting is 0.33 mm/sec. For $x = 0.8$, at which the structure has become *C*14, the quadrupole splitting has been reduced to about two-thirds of the value in the sample for $x = 0.4$ (*C*15 structure). The center shift is independent of Mn content within experimental error.

The increase in lattice constant when Fe in $ErFe_2$ is replaced by Mn is shown in Fig. 4. Also shown is the "hypothetical *C*15 lattice constant" for the *C*14 structure alloys, i.e., $a = (\sqrt{3}a^2c)^{1/3}$. It is clear that the transformation into the *C*14 structure is accompanied by a decrease in atomic size. The apparent Mn size is larger in the cubic material than in the hexagonal form, suggesting a higher valence state of Mn in the materials having the *C*14 structure. We thus ascribe a higher valence electron concentration to the *C*14 alloys, which is in keeping with the classic work of Laves and Witte (*8*) in the 1930's on the prototype Laves phase structures. They found, for example, that $MgCu_2$ (*C*15 structure) transforms into the *C*14 structure when monovalent Cu is replaced by di- or trivalent elements such as Zn or Al. The change takes place at a definite electron concentration, which they were able to relate to effects occurring when the Fermi surface begins to encounter the surfaces of the Brillouin Zone. Similar effects may be occurring in the present system, the ionization of Mn into a higher valence state giving rise to Fermi surface Brillouin Zone boundary interactions which generate the *C*14 structure.

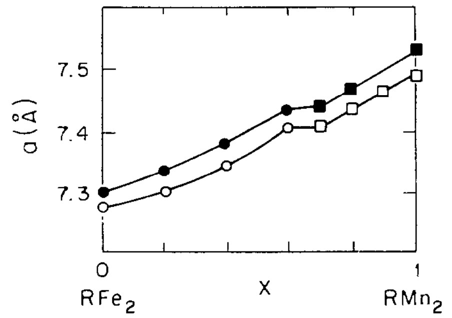

FIG. 4. Room-temperature lattice constants for $R(Fe_{1-x}Mn_x)_2$ ternaries. Open circles and squares are for $R = Er$; filled circles and squares are for $R = Ho$. Squares designate the hypothetical *C*15 lattice constant for materials which actually exist in the *C*14 structure.

Acknowledgment

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