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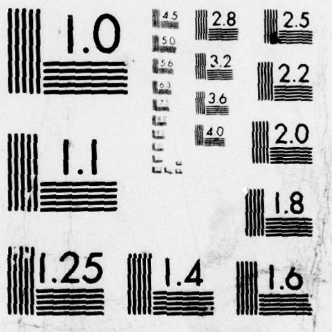

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MAGNETIC PROPERTIES OF SOME GADOLINIUM, ERBIUM, DYSPROSIUM, MANGANESE SUBSTITUTED SAMARIUM-2 COBALT-17 INTERMETALLIC COMPOUNDS

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ELECTRONICS TECHNOLOGY & DEVICES LABORATORY

August 1979

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The series of compounds (gadolinium, erbium, dysprosium)2-x, (manganese)y substituted samarium 2-x cobalt 17-y were studied with the object of developing permanent magnet materials having intrinsically temperature compensated magnetizations. The properties investigated were saturation magnetization, temperature coefficient of magnetization, and anisotropy field. The composition ranges studied were from x=0 to 0.6 and y=0 to 2. It was established that excellent temperature compensation could be achieved in these compounds in the temperature (cont'd)

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20. Abstract (cont'd)

range -50 to 150 C. The systematic variations of saturation magnetization and anisotropy field with gadolinium, erbium and dysprosium concentation for fixed values of the manganese concentration will be discussed.

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TABLE

FIGURES

MAGNETIC PROPERTIES OF SOME $Sm_{2-x}R_xCo_{17-y}Mn_y$ INTERMETALLIC COMPOUNDS

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INTRODUCTION

Current military requirements are leading to the development of a new generation of microwave and millimeter wave tubes whose magnetic circuits need permanent magnets with the following properties: energy products in excess of 30 MGOe, low reversible temperature coefficients of magnetization, α, and linear demagnetization curves. Rothwarf, Leupold and Jasper (1) have discussed approaches to the design of such magnetic circuits and the synthesis of suitable permanent magnet materials. Some of our preliminary efforts to attain compounds with such properties were also recently reported (2,3) and reviewed (4). In the present paper we review our earlier work and report new results on the use of heavy rare earth substituents for some samarium in an attempt to achieve intrinsically temperature compensated 2-17 magnets. Such an approach was first successfully applied to $SmCo_5$ by Benz, Laforce and Martin (5). The systems being reported on are $Sm_{2-x}R_xCo_{17-y}Mn_y$, where R=Gd, Er and Dy. The manganese is being used since we had previously found (6) that its presence in the quaternary system $Sm_2Mn(Co,Fe)_{16}$ significantly enhanced the anisotropy fields H_A over those measured for the corresponding compounds in the ternary system $Sm_2(Co,Fe)_{17}$. Also Nagel (7) found that using manganese or chromium substituents for cobalt in the Sm_2Co_{17} and $Sm_2(Co,Fe)_{17}$ compounds significantly enhances their coercivities and energy products. Thus, we have been investigating the magnetic properties of these systems with the expectation that the heavy rare earth substituents would yield low α's in compounds having their anisotropy fields enhanced by the manganese substituent.

EXPERIMENTAL

The experimental procedures used to determine the magnetization $\sigma_s(T)$, the temperature coefficient of magnetization, α, and the anisotropy field H_A have been described in detail elsewhere (2-4,8). We reiterate the experimental reproducibility of the various measurements. For the magnetization σ_s it was about ±1.5% in a maximum field of 15 kOe. The resultant α's have an uncertainty of ±15%/°C. The reproducibility for H_A when the material is saturated ($H_A < 100$ kOe) is about ±1.0%. The values for the extrapolated H_A's are ±2.5% for $100 < H_A < 125$ kOe, ±5.0% for $125 < H_A < 150$ kOe and ±8.0% for $H_A > 150$ kOe.

The α's for all the materials investigated are shown in Table 1 together with room temperature (300 K) saturation magnetization values σ_s and the anisotropy fields H_A at 273 K for the various compounds. Approximate $4\pi M_s$ values derived from σ's are also tabulated. The densities necessary to make this conversion were obtained by assuming that the volumes per unit cell of all compounds were the same as that for Sm_2Co_{17} and scaling the mass per unit cell to take into account the atomic masses of the various substituents. This was done because our preliminary x-ray diffraction results indicate that unit cell volumes of all the compounds are the same to within about one percent. The densities calculated in this manner varied from 8.61 to 8.72 g/cm^3.

RESULTS AND DISCUSSION

It was intended that the $Sm_{2-x}R_xCo_{17-y}Mn_y$ systems would be investigated for the compositions x=0, 0.2, 0.4 and 0.6 and y=0, 1 and 2. To date, the complete set of data has only been obtained for the gadolinium-substituted system. The results for the various compounds studied so far are listed in Table 1 and their various correlations are shown in Figs. 1-5. For purposes of clarity the results for the gadolinium compounds will be discussed first in section A. Section B will then compare the three sets of compounds for the case y=0 where all the data are complete.

A. The $Sm_{2-x}Gd_xCo_{17-y}Mn_y$ Systems

The magnetization results for the gadolinium compounds are shown in Fig. 1 for the x=0, 0.2, 0.4 and 0.6 samples. From such curves an average reversible temperature coefficient of magnetization was obtained, where α is defined as

Table 1. Saturation Magnetizations, Anisotropy Fields and Average Temperature Coefficients for the Systems $Sm_{2-x}R_xCo_{17-y}Mn_y$ (R=Gd, Er, Dy).

Composition y	x	σ_s 300 K (emu/g)	$4\pi M_s$ 300 K (kG)	H_A 273 K (kOe)	α_L 225-300 K (%/K)	α_H 300-425 K (%/K)
			$Sm_{2-x}Gd_xCo_{17-y}Mn_y$			
0.	0.0	117	12.7	85.3	-0.010	-0.011
	0.2	107	11.6	82.1	-0.010	-0.010
	0.4	96.2	10.5	78.7	0.000	+0.015
	0.6	97.3	10.6	66.5	0.000	+0.015
	2.0	67.0*	7.50*	--	+0.069*	+0.074*
1,	0.0	118	12.7	109	-0.021	-0.027
	0.2	110	11.9	98.5	-0.019	-0.017
	0.4	105	11.4	88.2	0.000	-0.006
	0.6	101	10.9	85.0	-0.002	-0.019
2,	0.0	114	12.3	90.0	-0.032	-0.038
	0.2	106	11.4	92.7	-0.022	-0.021
	0.4	91.0	9.82	86.7	-0.020	-0.019
	0.6	96.3	10.4	109	-0.029	-0.029
			$Sm_{2-x}Er_xCo_{17-y}Mn_y$			
0,	0.0	117	12.7	85.3	-0.010	-0.011
	0.2	99.8	10.9	81.4	0.000	0.000
	0.4	105	11.5	67.5	+0.007	+0.002
	0.6	105	11.5	64.0	+0.015	+0.001
	2.0	90.2†	10.1†	--	+0.099†	+0.045†
1,	0.0	117	12.7	109	-0.021	-0.027
	0.2	103	11.2	116	-0.006	-0.019
2,	0.0	114	12.3	90.0	-0.032	-0.038
	0.2	102	11.1	106	-0.031	-0.038
	0.4	107	11.6	105	-0.120	-0.018
			$Sm_{2-x}Dy_xCo_{17}$			
0,	0.0	117	12.7	85.3	-0.010	-0.011
	0.2	114	12.5	69.8	0.000	0.000
	0.4	105	11.5	49.2	+0.016	+0.016
	0.6	95.1	11.4	60.0	+0.014	+0.014
	2.0	64.4*	7.14*	--	+0.188*	+0.171*

* R. Lemaire, Cobalt 33, 301 (1966)

† A.E. Miller, T. D'Silva and H. Rodrigues, IEEE Trans. Magnetics, MAG-12, 1066 (1976).

$$\alpha = \frac{\Delta M}{M_1 \Delta T} \times 100\% = \frac{M(T_2) - M(T_1)}{M(T_1)\ (T_2 - T_1)} \times 100\ \% \qquad (1)$$

We chose to list α's for a high temperature region, α_H, where 300 K < T < 425 K and for a low temperature region, α_L, where 225 K < T < 300 K. In each case T_1 was taken to be 300 K. ΔM was always chosen as the maximum magnetization change over the temperature interval ΔT.

In Fig. 1 the set of $4\pi M_s(T)$ curves for the $Sm_{2-x}Gd_xCo_{17-y}Mn_y$ compounds are shown. It is clear that the substitution of gadolinium dramatically reduces the magnitude of the slopes of the curves for the cases where y=0 and 1, especially for the substitution of $Gd_{0.4}$ and $Gd_{0.6}$. In some cases the slopes are changed from negative to positive as more gadolinium is substituted. These results demonstrate the validity of using heavy lanthanide substituents for lowering the magnitude of α in the 2-17-based compounds.

The α_L and α_H values are plotted in Fig. 2 as a function of gadolinium concentration for the various fixed values of the manganese substituent. Making use of magnetization data for Gd_2Co_{17} (9) and our data for Sm_2Co_{17}, we have plotted the linear variation of α with Gd concentration expected from a simple additivity approximation (1) for the y=0 case. Within experimental error this approximation seems to have some validity. However, the shapes of the y≠0 curves, which are similar to the y=0 case, lead one to believe that the functional dependence of α with gadolinium concentration may be more complex. From a practical standpoint it seems that the compound $Sm_{1.6}Gd_{0.4}Co_{16}Mn$ would furnish a good intrinsically temperature compensated magnet material for the temperature range of military interest, 225 K < T < 425 K.

The final choice of an optimal alloy to achieve a zero temperature coefficient (ZTC) material is influenced by the variation of magnetization and anisotropy, as well as ultimately the coercivity and maximum energy product with manganese and gadolinium concentration. In Fig. 3 we plot the variation with temperature of $4\pi M_s$, and H_A with manganese concentration for the different gadolinium concentrations at temperatures of 2.3 and 273 K. From Fig. 3A it is clear that there is a monotonic decrease in $4\pi M_s$ as the gadolinium substituent is increased. This behavior is what one expects from the antiferromagnetic coupling of gadolinium to the other moments in the system. For a given x, however, a shallow maximum occurs in the 273 K or 300 K curves for the substitution of one manganese atom for cobalt. A similar monotonic decrease is apparent from Fig. 3B for the variation of H_A with gadolinium concentration and with the exception of x=0.6 a maximum also occurs for the case of one manganese atom substituted for cobalt. The microscopic rationale for these trends is presently not well

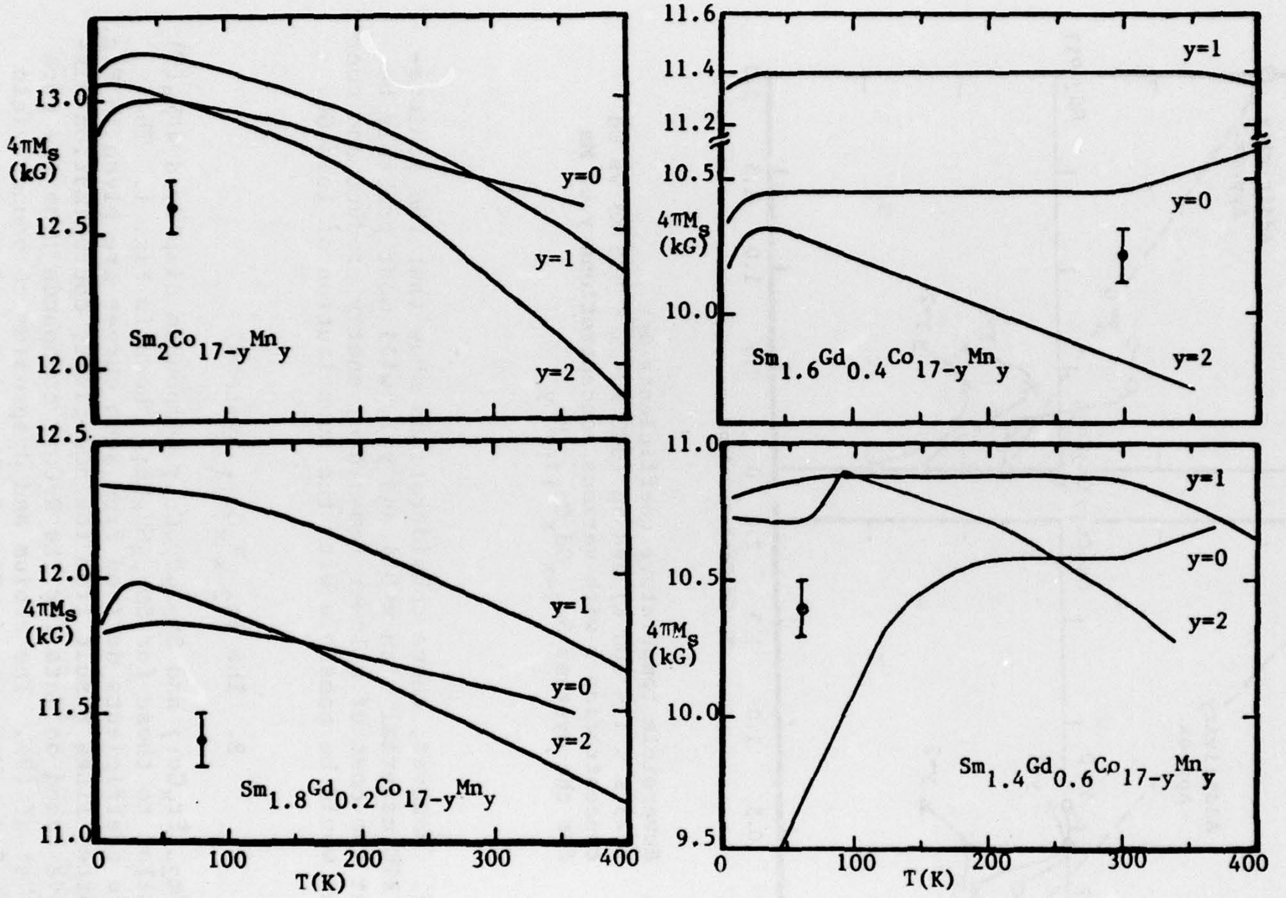

Figure 1. Saturation magnetization $4\pi M_s$ vs temperature for the $Sm_{2-x}Gd_xCo_{17-y}Mn_y$ systems (for x=0, 0.2, 0.4 and 0.6; y=0, 1, 2). Data obtained with an applied field of 15 kOe.

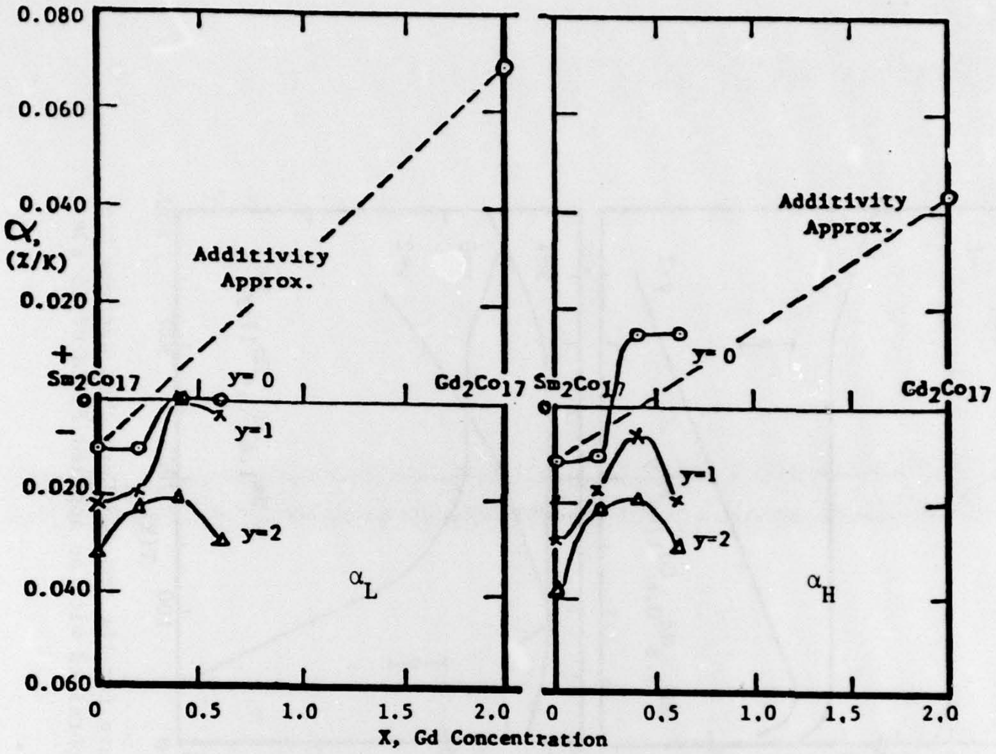

Figure 2. Reversible temperature coefficients α_L (225 K < T < 300 K) and α_H (300 K < T < 425 K) vs Gd concentration x with various concentrations y of Mn for the systems $Sm_{2-x}Gd_xCo_{17-y}Mn_y$.

understood. However, these considerations show that the achievement of a ZTC material with x=0.4 and y=1, will most probably be attained at the cost of a lower remanence, energy product and coercivity than would be possible with the substitution of less Gd.

B. The $Sm_{2-x}R_xCo_{17}$ Systems

The $Sm_{2-x}Er_xCo_{17}$ and $Sm_{2-x}Dy_xCo_{17}$ compounds displayed $4\pi M_s(T)$ curves similar to those for $Sm_{2-x}Gd_xCo_{17}$ shown in Fig. 1. The temperature coefficients derived from such curves are given in Fig. 4. The dotted lines result from the additivity approximation discussed above based on data for the R_2Co_{17} compounds from the work of Lemaire et al (9). The erbium and dysprosium compounds yield ZTC's for x=0.2. However, in Fig. 5 where $4\pi M_s$ and H_A data are shown, it may be seen that certain trade-offs exist. The $4\pi M_s$

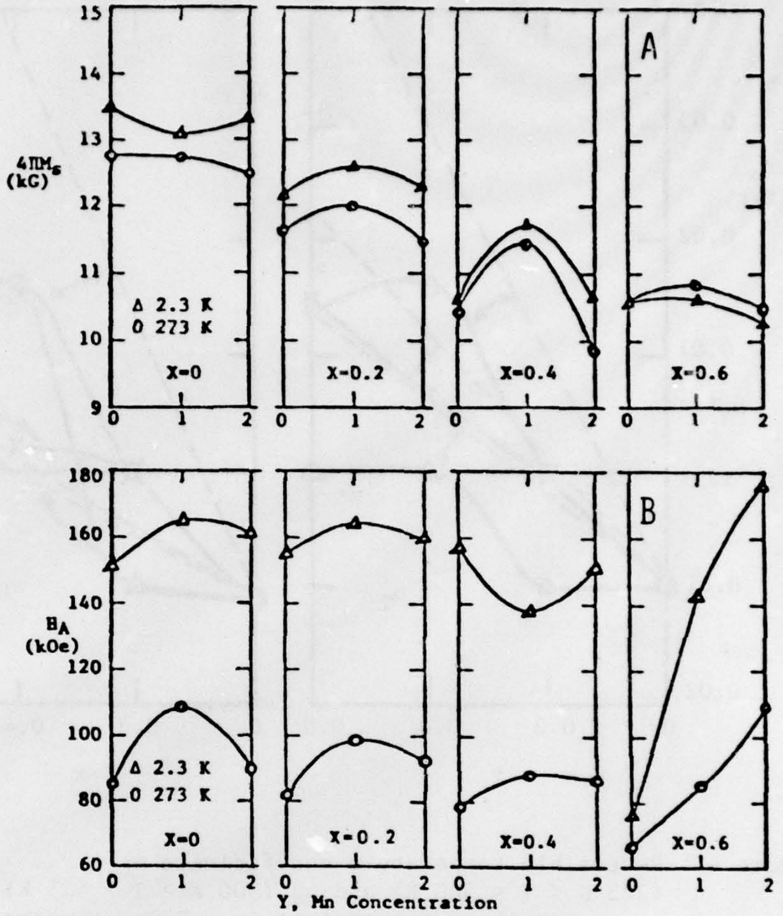

Figure 3. (A) Saturation magnetization $4\pi M_s$ and (B) anisotropy field H_A vs Mn concentration y for the sets of compounds $Sm_{2-x}Gd_xCo_{17-y}Mn_y$ (where x=0, 0.2, 0.4, 0.6) at temperatures 2.3 K (Δ) and 273 K (O). $4\pi M_s$ and H_A data were taken in applied fields up to 100 kOe.

for the dysprosium compound is not reduced as much as it is for the erbium compound. On the other hand, the dysprosium compound shows a greater decline in H_A than does the erbium. A preliminary result for the erbium system indicates that the substitution of one manganese atom for cobalt significantly enhances H_A from 85 kOe to 109 kOe (see Table 1) while maintaining relatively low α's. This result makes the $Sm_{1.8}Er_{0.2}Co_{16}Mn$ compound an attractive candidate for magnet development. Whether the addition of manganese to the dysprosium compound will produce similar results remains to be determined.

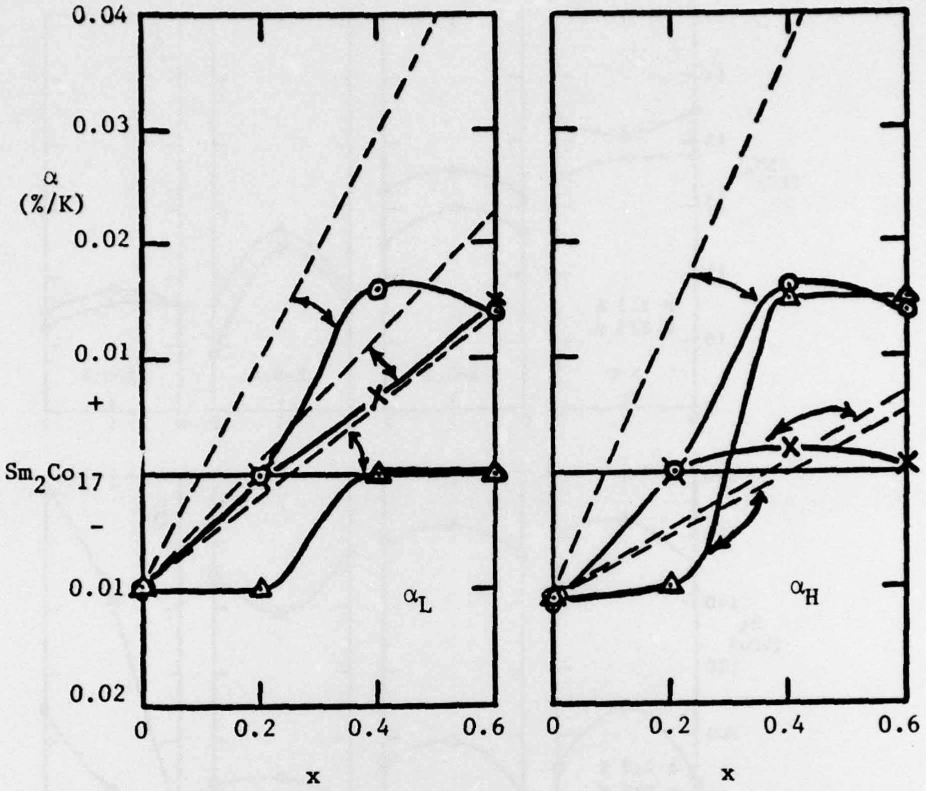

Figure 4. Reversible temperature coefficients α_L (225 K < T < 300 K) and α_H (300 K > T > 425 K) vs Gd concentration x for systems $Sm_{2-x}R_xCo_{17}$, where R = Gd(Δ), Er(x), and Dy(◉).

The dashed lines in Fig. 5A represent the $4\pi M_s$ values obtained by suitably summing the moments of the constituent atoms. In so doing we assumed the rare earth free atom moments (Sm, 0.714 μ_B; Gd, 7.0 μ_B; Er, 9.0 μ_B; and Dy, 10.0 μ_B) given by Kirchmayer (10) and the cobalt moment (1.65 μ_B) given by Streever (11) for cobalt in the Nd_2Co_{17} compound. It was further assumed that the heavy lanthanides coupled antiferromagnetically with the samarium and cobalt. The trends seem to be correct. For the dysprosium system the theoretical curve parallels the low temperature results and agrees with them to within experimental error. The deviations for the other systems probably reflect crystal field and/or band structure effects which require further theoretical effort for their clarification. The same can be said for the various systematic trends seen in the figure.

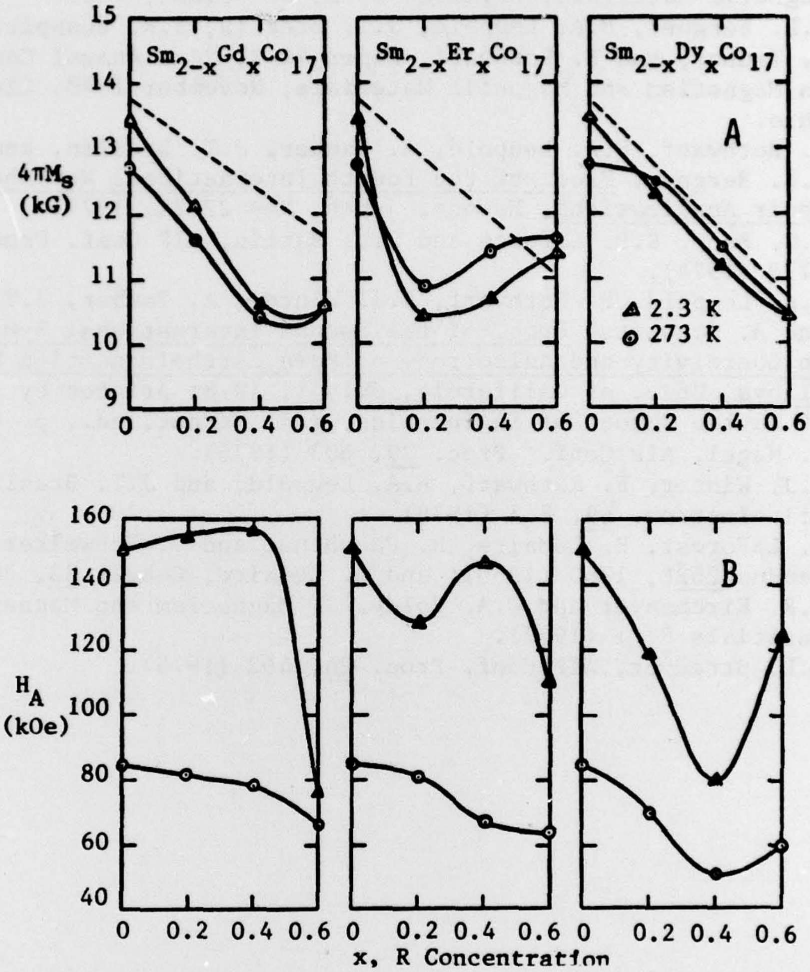

Figure 5. (A) Saturation magnetization $4\pi M_s$ and (B) anisotropy field H_A vs R concentration x for the compounds $Sm_{2-x}R_xCo_{17}$ at temperatures 2.3 K (Δ) and 273 K (O). $4\pi M_s$ and H_A data were taken in applied fields up to 100 kOe.

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