Magnetic characteristics of $RCo_{13-x}Si_x$ alloys (R=La, Pr, Nd, Gd, and Dy)

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The magnetism of $LaCo_{13}$-type alloys such as $LaCo_{13}$, $PrCo_{13-x}Si_x$, etc., has recently received considerable attention as potentially useful magnetic materials. The present study is concerned with $RCo_{13-x}Si_x$ where R=La, Pr, Nd, Gd or Dy. [S0021-8979(96)33508-2]

I. INTRODUCTION

The alloys $LaCo_{13}$ and $La(Co,Fe)_{13}$ have a high content of $3d$ elements. The high concentration of $3d$ elements leads to a large magnetization and, in some cases, a high T_C. Because of these properties these alloys have attracted attention as potential high energy permanent magnet materials.[1–6] In earlier studies from this laboratory, Ido *et al.* have studied $La(Co,Fe,Al)_{13}$ (Ref. 1) and Huang *et al.* have studied $PrCo_{13-x}Si_x$.[7] The earlier works have been extended in the present study to include the ternaries $RCo_{13-x}Si_x$, in which R=Nd, Gd, and Dy.

II. EXPERIMENTAL DETAILS

The ternary alloys were prepared by induction melting under argon, after which they were heat treated at 1273 K for about one week. X-ray diffraction (XRD) with Cu radiation was used to determine crystal structure, lattice parameters, and the phases present.

The magnetic properties (M and T_C) were measured using vibrating sample magnetometers (VSM) at temperatures ranging from 10 to 1173 K and fields ranging from 500 Oe to 17 kOe. The TMA measurements were made in such a manner [low applied field (500 Oe) and variable heating rate] to provide the most reliable information about the phases present and the values of T_C and to clearly identify the spin reorientation

III. RESULTS AND DISCUSSION

A very large body of data was acquired. Due to space limitations, only a few representative data can be presented. The results are exemplified by the data given in Tables I and II and Figs. 1–7.

A. Phases formed and structural information

Information concerning the phase relationships is obtained by XRD measurements such as those shown in Figs. 1 and 2. The phase relationships are rather similar for the five systems studied: (1) At low Si content, $1.5 \leqslant x \leqslant 2.0$, the alloys form in the fcc $NaZn_{13}$ structure. (2) At high Si content, $3.5 \leqslant x \leqslant 4.5$, they form in the body-centered tetragonal (bct) $Ce_2Ni_{17}Si_9$ structure. (3) At intermediate Si concentrations the systems are a mixture of fcc and bct alloys. There are, however, some exceptions to these generalizations: (1) The fcc phase forms at $x=0$–2 for R=La. (2) The fcc structure begins to form at $x=1.5$ for R=Pr, whereas it forms only for

TABLE I. Phases present and structural information for $RCo_{13-x}Si_x$ alloys (R=La, Pr, Nd, Gd, Dy).

Phases present				Lattice parameters (main phase)			
R	x	Main	Minor	a (A)	c (A)	c/a	V (A^3)
La	0	fcc[a]		11.340			1458.27
	1.0	fcc		11.325			1452.49
	2.0	fcc		11.295			1440.98
	2.5	fcc	bct				
	3.0	bct	fcc	7.871	11.523	1.464	713.88
	3.5	bct[b]	(fcc->0)	7.851	11.551	1.471	711.98
	4.0	bct		7.827	11.567	1.478	708.63
	4.5	bct	Co_2Si	7.834	11.592	1.478	711.42
Pr	2.0	fcc		11.259			
	2.5	fcc	bct				
	3.0	bct	fcc				
	3.5	bct	fcc	7.821	11.500	1.470	730.43
	4.0	bct		7.805	11.539	1.478	702.93
	4.5	bct	Co_2Si	7.826	11.566	1.478	708.37
Nd	3.0	bct	fcc, 1:11[c]	7.834	11.459	1.462	703.25
	3.5	bct	fcc	7.828	11.489	1.470	702.22
	4.0	bct		7.788	11.519	1.479	698.66
	4.5	bct	Co_2Si	7.797	11.552	1.481	702.28
Gd	3.5	bct	1:11				
	4.0	bct	fcc, Co_2Si	7.773	11.495	1.478	694.52
Dy	3.5	bct	1:11				
	4.0	bct	Co_2Si	7.758	11.491	1.481	691.66

[a]fcc signifies the $NaZn_{13}$ structure.
[b]bct signifies the $Ce_2Ni_{17}Si_9$ structure.
[c]The 1:11 signifies the $BaCd_{11}$ structure.

TABLE II. Magnetic properties of $RCo_{13-x}Si_x$ (R=La, Pr, Nd, Gd, and Dy).

			M (emu/g)		$M(\mu_B$/f.u.)	M(Co,R)	T_{sr}	H_c (Oe)
R	x	T_c (K)	293 K	10 K	10 K	μ_B/atom	(K)	10 K
La	0	1297	126.0	131.4	21.3	1.64		
	1.0	1050	106.0	108.0	16.9	1.41		
	2.0	880	75.9	80.2	12.1	1.10		
	3.0	295,880	26.6	41.4	6.0	0.6		
	3.5	200,880	4.3	24.0	3.4	0.4		
	4.0	40	0.33	2.24	0.3	0.03		
	4.5	⋯	0.23	0.28	0.04	⋯		
Pr	2.0	903	78.1	92.7	14.0	1.9		
	2.5	~295,903	54.4	73.7	11.0		~28	900
	3.0	~290,903	29.9	55.2	8.1	2.1	~28	700
	3.5	~70,903	10.1	37.2	5.3	1.9	~55	600
	4.0	20	1.7	19.2	2.7	2.4	⋯	
	4.5	20	1.4	15.8	2.2	2.2		
Nd	3.0	~300,908	29.6	53.9	7.9	1.9	~45	500
	3.5	225,908	5.8	40.7	5.8	2.4	~48	400
	4.0	20	0.7	17.8	2.5	2.2		
Gd	3.5	70,483	8.6	23.1	3.4	6.8		
	4.0	50,600	7.9	26.5	3.8	4.1		
Dy	3.5	55,490	8.5	37.7	5.5	8.9	⋯	750
	4.0	45	2.2	36.8	5.3	5.8	⋯	240

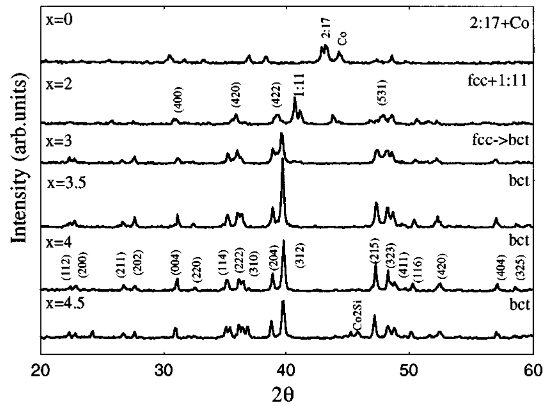

FIG. 2. XRD pattern for $NaCo_{13-x}Si_x$.

x exceeding 3–3.5 for the heavier rare earths, Nd, Gd, or Dy. Also as noted in Table I, some of the alloys contained minor amounts of other phases: 2:17, 1:11, and Co_2Si. The lattice parameters (Table I) show that Si doping causes a shrinkage of the lattice.

In summary, the ternaries (and $LaCo_{13}$) are fcc for low Si content and one bct at high Si content. Further details are given in Table I.

B. Magnetic properties

Magnetization results are given in Figs. 3–7 and in Table II. From the results presented, it is to be noted that $LaCo_{13}$, which is fcc, is a strongly ferromagnetic material (moment =131 emu/g) with a high T_C, 1297 K. It thus satisfies two of the requirements for a high energy permanent magnet material. However, it lacks a third requirement—a uniaxial crystal structure. The present study (and earlier studies) shows that the third requirement can be induced by Si doping.[1,6,7] Unfortunately, however, as indicated in Figs. 3–7 and in Table II, the tetragonal materials have a low T_C—room temperature or below. The fcc alloys have a T_C ranging from 880 K (for $LaCo_{11}Si_2$) to 1297 K for $LaCo_{13}$. For a given Si content, the T_C of the fcc phase is dependent on the nature of R. As expected, the dominant interaction is the Co–Co interaction.

In regard to the magnetic moment, there is a decrease as Si replaces Co, but the decrease is larger than expected due to the simple dilution of the Co sublattices. The decrease begins in the fcc alloys and continues in the bct alloys. The bct alloys have small moments, <10 emu/g, as measured at ~10 K.

The TMA for bct alloys with R=Pr and Nd show clear indications of a spin reorientation when cooled to tempera tures in the liquid hydrogen range (Figs. 4 and 5). As shown in Table II, $T_{sr}=55$ and 48 K for $PrCo_{9.5}Si_{3.5}$ and $NdCo_{9.5}Si_{3.5}$, respectively. No spin reorientation was observed for the La, Gd, and Dy ternaries. This is as expected for $La(Co,Si)_{13}$—since La carries no moment—and for $Gd(Co,Si)_{13}$—in which the rare earth is spherical and hence is isotropic. It is unclear why there is no indication of spin

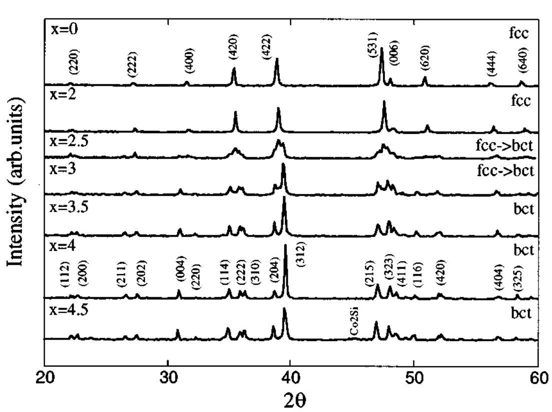

FIG. 1. XRD patterns for $LaCo_{13-x}Si_x$. The splitting of the 422 peak at $2\theta\sim39°$ is a clear indication of the transformation from cubic to tetragonal symmetry.

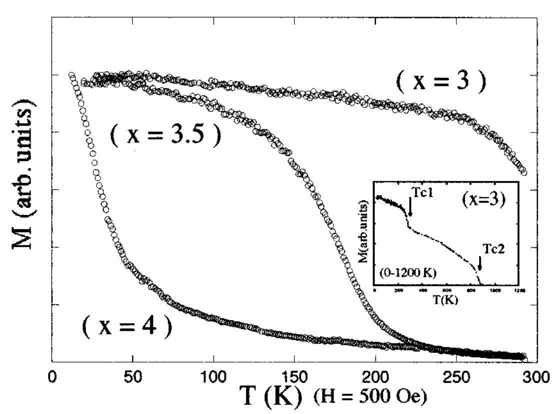

FIG. 3. M vs T for three representative bct $La(Co,Si)_{13}$ alloys. The alloys with $x=3.5$ and 4 are nearly single-phase material. Their Curie temperatures are about 200 and 40 K, respectively. The alloy with $x=3$ is a two-phase system composed of fcc and bct alloys (see Table I). The presence of the fcc impurity phase strongly affects the magnetization of the bct phase.

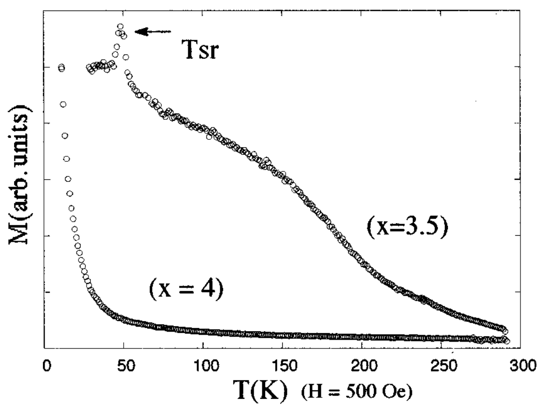

FIG. 4. M vs T for two representative $Nd(Co,Si)_{13}$ alloys. The T_C's for $NdCo_9Si_4$ and $PrCo_9Si_4$ are essentially identical. The spin reorientation at ~50 K is clearly evident.

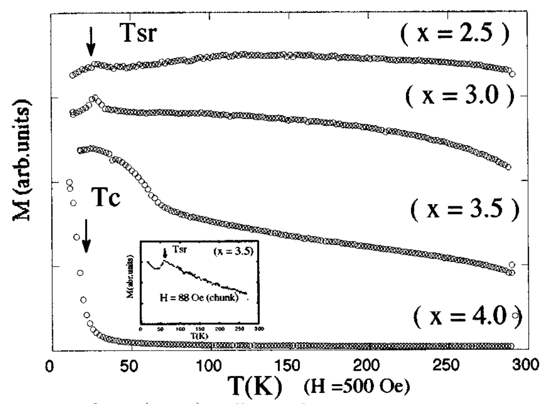

FIG. 5. M vs T for $Pr(Co,Si)_{13}$ alloys. The spin reorientation at ~28 K is clearly evident for x=2.5–3.5.

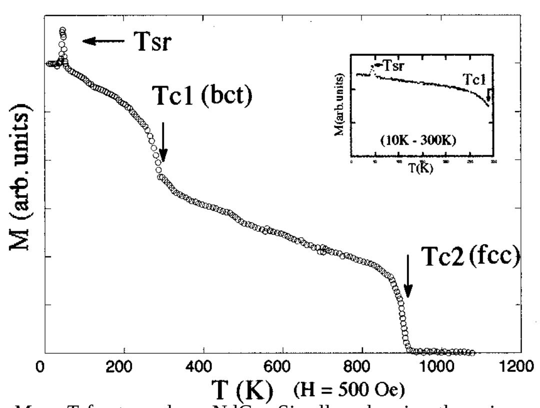

FIG. 6. M vs T for two-phase $NdCo_{10}Si_3$ alloy showing the spin reorientation at ~45 K and the T_C's for the bct and fcc components.

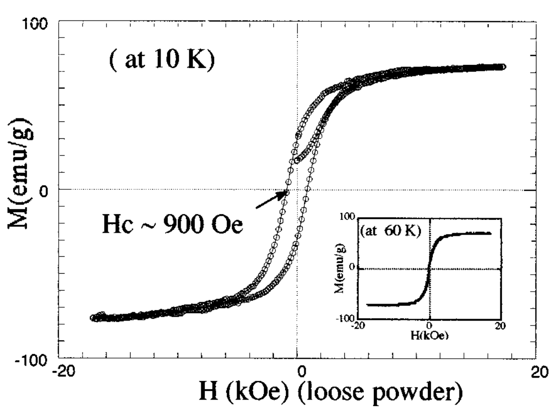

FIG. 7. Hysteretic behavior of $PrCo_{10.5}Si_{2.5}$, showing significant coercivity for $T<T_{sr}$, but not for $T>T_{sr}$.

rotation for the Dy-containing ternaries. Boltich, Pedziwiatr, and Wallace showed[8] some years ago that spin reorientation in rare earth–d-transition metal alloys occurs as a result of a complex interplay between the crystal field interaction for the R sublattice and exchange primarily involving the d sublattice. The temperature of the spin reorientation and the shape of the aberration in the TMA depend on the details of this interplay. Perhaps in $Dy(Co,Si)_{13}$ the spin reorientation takes place at a temperature lower than that covered in this study. Interestingly, the Dy alloy exhibits coercivity in its hysteresis loop even though it does not indicate spin reorientation in its M vs T plot.

Hysteresis loops were measured at temperatures above and below T_{sr} for the ternaries in loose powder form. A representative loop (for $PrCo_{10.5}Si_{2.5}$) is shown in Fig. 7. There is negligible coercivity for $T>T_{sr}$ but appreciable coercivity for $T<T_{sr}$. This suggests that magnetization is along the c axis below T_{sr} and shifts to the ab plane above $T>T_{sr}$.

IV. CONCLUSION

$LaCo_{13}$ exists in the fcc $NaZn_{13}$ structure. The corresponding Pr alloy also forms in the same structure if a small portion of the Co is replaced by Si. At higher Si content, all the systems adopt the bct $Ce_2Ni_{17}Si_9$ structure. The fcc alloys have high T_C and are strongly magnetic. The bct alloys are weakly magnetic with T_C at or below room temperature. $Pr(Co,Si)_{13}$ and $Nd(Co,Si)_{13}$ exhibit spin reorientation at ~60 and 50 K, respectively. Hysteresis results suggest a uniaxial material at temperatures below T_{sr} and ab plane anisotropy for $T>T_{sr}$. Si doping stabilizes the $NaZn_{13}$ structure in $R(Co,Si)_{13}$ alloys. This does not appear to be exclusively a size effect.

ACKNOWLEDGMENTS

The authors express appreciation to Dr. B. M. Ma of Rhone Poulenc for gifts of rare earth metal for use in this study. This work was supported by U.S. Army Research Office.

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