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STRUCTURE AND MAGNETIC PROPERTIES OF $LaCo_{13}$-BASED ALLOYS *

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The structure and magnetic properties of two series of $LaCo_{13}$-based alloys, $LaCo_{13-x}Fe_x$ ($0 \leq x \leq 6$) and $La_{1-x}R_x(Co, Fe)_{13}$ ($x = 0.1, 0.2$; R=Y, Ge, Pr, Nd Sm, Gd, Tb, Dy, Ho, Er, and Yb), are studied by X-ray diffraction and magnetic measurements. In the above-mentioned composotions, all the samples display a structure of $NaZn_{13}$ type (space group: $Fm3c$). In $LaCo_{13-x}Fe_x$ system, as the iron content increases, its Curie temperature decreases, while the magnetic moment per 3d atom increases. This may be explained by a rigid band model. In the other alloy system, the Curie temperature goes through a maxium at R=Gd, and this reflects the influence of $R-T$ interaction. It is also observed that saturation magnetization varies with R and gets lower when R is a heavy rare earth element. The contribution of R is close to that of a free-ion moment. $La_{0.9}Pr_{0.1}Co_9Fe_4$ has the largest value $29\mu_B$/f.u.

PACC: 7530; 7550B.

I. INTRODUCTION

The magnetic compounds composed of rare earth (R) and transition metal (T), such as $Nd_2Fe_{14}B$ and $Sm_2Fe_{17}N_x$, have been a focus of research for a long time. On the other hand, the compound $LaCo_{13}$ has the highest content of 3d metal in all known rare earth intermetallics, with a Curie temperature 1318K[1,2], so it is a potential starting compound for magnetic materials. But it is cubic, with a $NaZn_{13}$ type structure[3], and possesses a rather low anisotropy. In spite of this, the compound can also be used to study the magnetic properties and other problems[4-6].

We here report the structures and magnetic properties of two series of $LaCo_{13}$-based alloys, $LaCo_{13-x}Fe_x$ ($0 \leq x \leq 6$) and $La_{1-x}R_x(Co,Fe)_{13}$ (x=0.1, 0.2; R=Y, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, and Yb), studied by means of X-ray diffraction and magnetic measurements. As the iron content increases in $LaCo_{13-x}Fe_x$ system, the Curie temperature decreases whereas magnetic moment per 3d atom increases. And in the other system, the saturation magnetization varies with rare earth elements.

II. EXPERIMENTAL

The alloy samples $LaCo_{13-x}Fe_x$ (x=0.0, 0.5, 1.0, 1.5, 2.0, 3.0, ... , 9.0) and $La_{1-x}R_xCo_9Fe_4$ (x=0.1, 0.2, 0.3; R=Y, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er and Yb) were first arc-melted under an argon atomsphere from the starting materials R, Fe, and Co with purity of 99.5%, 99.9% and 99.9%, respectively. For homogenization the samples were remelted several times

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and then wrapped in tantalum foil and annealed at 950°C for 30 days in a quartz tube evacuated to 10^{-3} Torr. The samples were confirmed to be of a $NaZn_{13}$ structure by X-ray diffraction.

The magnetization at 77K was measured by extracting sample magnetometer and Curie temperature by magnetic balance. The highest temperature of magnetic balance is 950°C, so the T_C values cannot be obtained from our measurement when $x \leq 2$ in $LaCo_{13-x}Fe_x$.

III. RESULTS AND DISCUSSION

A. Structure and lattice constants

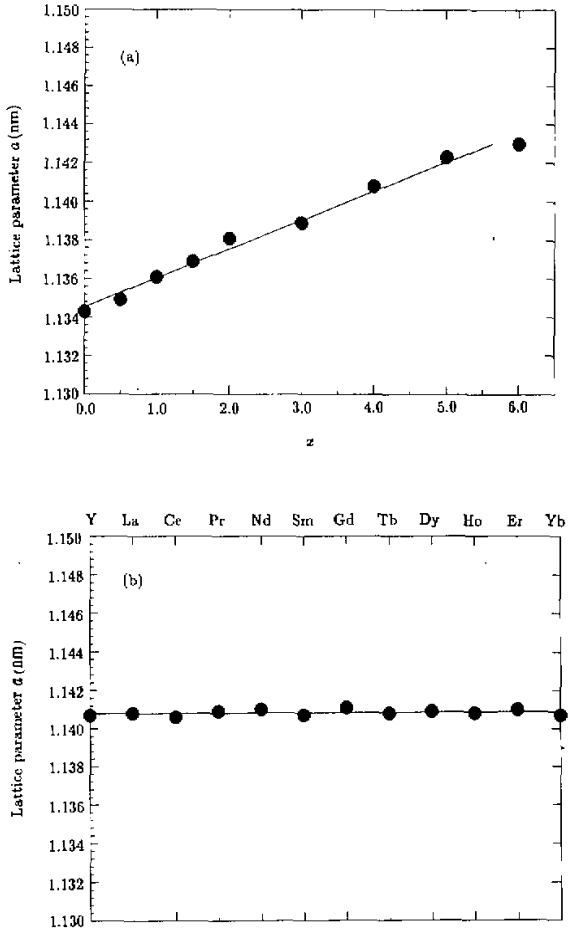

Fig. 1. The dependence of lattice constants on concentration of Fe in $LaCo_{13-x}Fe_x$ (a) and of R in $La_{1-x}R_x(Co,Fe)_{13}$ (b) alloys.

The compound $LaCo_{13}$ has a cubic $NaZn_{13}$ structure with $Fm3c$ space-group symmetry. In Wyckoff notation, La occupies the site 8(a), Co has two inequivalent sites: 8(b) and 96(i), the coordinates of these sites are (1/4, 1/4, 1/4), (0, 0, 0) and (0, 0.1806, 0.1192), respectively. X-ray diffraction confirmed that in $LaCo_{13-x}Fe_x$ the structure occurs in $NaZn_{13}$ type when $x \leq 6$, and its lattice constants increase slightly as x increases (Fig. 1(a)). The atomic radii of Fe and Co are 0.127nm and 0.125nm[7], respectively. The substitution of Co by Fe increases the average atomic radius, then the lattice constants increase. It is difficult to distinguish between the contributions from Fe and from Co in X-ray diffraction pattern due to their close atomic scattering factors. And taking the similarity of electron structures of Fe and Co into consideration, we treat them as an average transition element occupying the two inequivalent sites 8(b) and 96(i) randomly in some case. In the other system, $La_{1-x}R_x(Co_9Fe_4)$, we can obtain single phase samples as $x < 0.3$. La and another rare earth element (R) occupy the site 8(a) in $NaZn_{13}$ structure. The lattice constants are almost unchanged in the samples of x=0.1 (Fig. 1(b)) and it may indicate that the slight difference of rare earth elements at site 8(a) has less effect on lattice constant. Except La, all the other elements in lanthanum series cannot form compounds with Co or Fe in $NaZn_{13}$ type, so that the solid solubility is rather small.

B. Curie temperature and magnetic moments in $LaCo_{13-x}Fe_x$ alloys

The dependence of Curie temperature T_C and magnetic moment per 3d atom on the concentration of iron in $LaCo_{1-x}Fe_x$ alloys are shown in Fig.2. As x increases, the T_C decreases obvisouly while the magnetic moment increases.

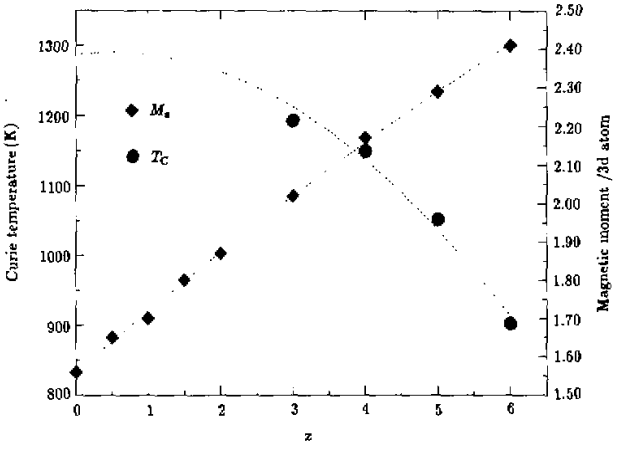

Fig. 2. The dependence of Curie temperature T_C and magnetic moment per 3d atom M_{3d} on the concentration of iron in $LaCo_{13-x}Fe_x$ alloys.

The variation of magnetic moment with the concentration of iron is similar to that in compounds of $La(Fe_{1-x}Co_x)_n$, $Y(Fe_{1-x}Ni_x)_n$ and $Y(Co_{1-x}Ni_x)_n$ (n=2, 3, 3.5, 5, 8.5)[8,9] and it can be explained by a rigid band model taking into consideration the number of

3d electrons. In $LaCo_{13-x}Fe_x$ alloys, the 3d electrons of Co and Fe share a common 3d band. When x=0 ($LaCo_{13}$), the spin-up subband is filled while the spin-down subband is unsatutated (illustrated in Fig.3(a)). As the substitution of Co by Fe increases, the number of 3d electron decreases, while vacancy also appears in the spin-up subband, and Fermi level gets lower (Fig.3(b)); the net magnetic moment (the difference of shadowed area in Fig.3) increases.

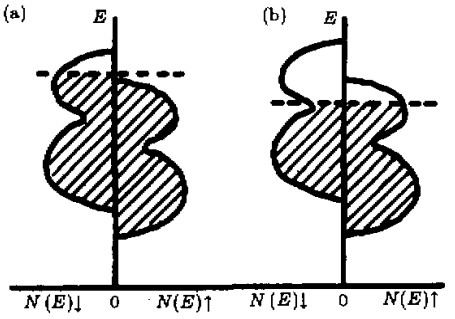

Fig. 3. An illustration of the density of states of 3d electron with spin-up and spin-down subband (E_F is Fermi level).

The Curie temperature in $R-T$ compounds is primarily determined by $R-T$ and $T-T$ interactions. If the $T-T$ distance is too short, the interaction will be antiferromagnetic and have a negative influence on Curie temperature, as in the case of dumbbell of iron atoms in R_2Fe_{17} compounds[10]. On the other hand, an extremely large $T-T$ distance is also a negative factor for T_C, as in the case of the nitrogenation of $LaCo_{13}$. Huang et al[6] discovered that the volume of $LaCo_{13}$ increases 9.9% after nitrogenation but T_C decreases by about 50% and magnetic moment decreases by 30%. It seems that the average distance 0.254nm[11] in $LaCo_{13}$ may be the best $T-T$ distance for T_C. In our alloys, the lattice constant increases and the $T-T$ distance may differ from the perfect value, so T_c gets lower. In addition, the difference between Fe–Fe interaction and Co–Co interaction also has influence on T_C.

C. Curie temperature and saturation moment in $La_{1-x}R_x(Co,Fe)_{13}$ alloys

The dependence of Curie temperature T_c and magnetic moments M_s on rare earth element R is shown in Fig.4. The Curie temperatures reach a maximum at R=Gd and fall on both sides. In these alloys, lattice constants are almost the same, and $T-T$ interaction is also unchanged. The main reason for the change of T_C is the $R-T$ interaction. But it is weaker compared to $T-T$ interaction. So the change of T_C is rather small when R changes from Y to Yb except R=Gd. For the element of Gd, its configuration is a half-filled shell with seven unpaired 4f electrons, and therefore an obvious influence on T_C was displayed.

It can be seen from Fig. 4 that the saturation moment is divided into two categories: the saturation values of the compounds of the light rare earth elements are considerably higher than those of the heavy rare earth ones. This is a consequence of the antiparallel coupling

between the rare earth spin moment and the iron moment, leading to a ferromagnetism in the former and to a ferrimagnetism in the latter. The saturation moment of the ferrimagnetic heavy rare earth compouds is $M_s = M_T - M_R$; by using the value of M_T derived from the moment of $LaCo_{13-x}Fe_x$, the contribution from rare earth element is found to be close to that of the free-ion moment. The moment of the sample with R=Pr, $29\mu_B$/f.u., is the highest one in these compounds. The low value of M_s with R=Ce is easily explained in terms of the tendency of Ce to adopt a valence state close to 4.

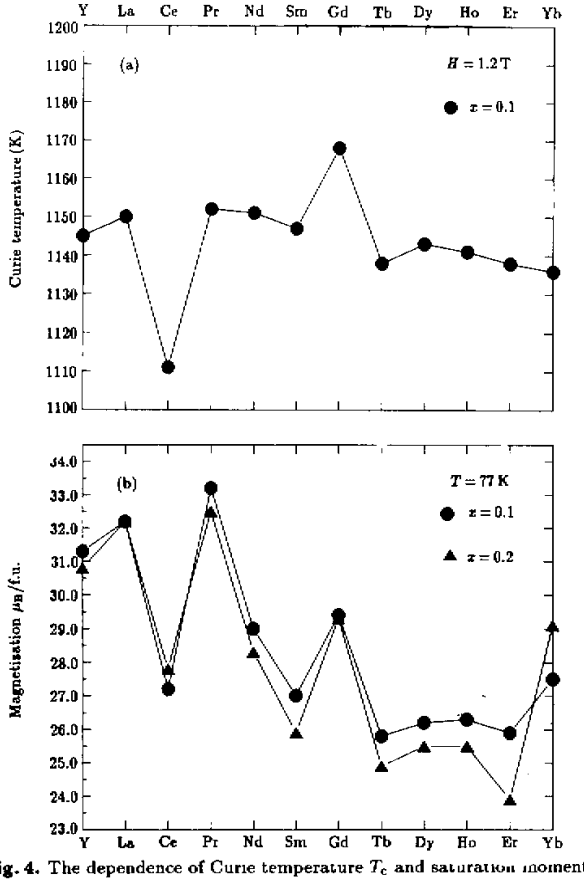

Fig. 4. The dependence of Curie temperature T_c and saturation moment M_s on rare earth element R in $La_{1-x}R_x(Co,Fe)_{13}$ alloys.

IV. CONCLUSION

In $LaCo_{13-x}Fe_x$ alloys, the substitution of Co by Fe enhances the magnetic moment while Curie temperature is still sufficiently high for application. The partial substitution of La by other rare earth elements has less effect on Curie temperature except Gd which enhances T_C obviously. The contribution of rare earth to saturation moment is close to that

of free-ion moment.

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