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2-17 La-Co-Fe Compounds; Synthesis and Magnetic Properties

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The effect of transition metals addition on the La-Co-Fe ternary system has been studied. $La_2(Co,Fe,M)_{17}$ was found to be synthesized with the addition of M=V, Mn, Nb, Mo, Ta, W. $La_2(Co,Fe,M)_{17}$ has rhombohedral (Th_2Zn_{17}) structure and saturation magnetization of 1.2-0.8T at room temperature, which increases with an increase in Fe content. The $La_2(Co,Fe,M)_{17}$; (M=Mn, Mo, W) have c-axis magnetizetion and anisotropic field of more than 1T.

1. INTRODUCTION

The magnetism of rare earth-transition metal compounds originates from the nature of 3d and 4f electrons in the compounds. The essence of the contributions of electrons to magnetic properties can be referred to electron-electron and electron-crystal field interactions.
In Ln-Co compounds, only La-Co system is lack of both 2-17 compound and 4f electron, so that the study of this system can offer some information available for considering the origin of formation of 2-17 compound and magnetic properties.
In this paper, synthesis of La_2Co_{17} was attempted by addition of various transition metal elements and their magnetic properties were investigated.

2. EXPERIMENTAL

Alloys in La-Co-Fe-M; (M=V, Cr, Mn, Zr, Nb, Mo, Hf, Ta, W) were prepared by rf melting furnace in purified Ar gas atmosphere, using >99.5% purity metals. The alloy ingots were pulverized to powder 2-5 μm in size, followed by compaction under a magnetic field. The compacts were sintered at 1413K-1473K for 2h in vacuum and homogenized at 1073K-1373K for 20h-45h in purified Ar atmosphere.
Analyses of crystal structure and measurements of magnetic properties were carried out as mentioned in previous paper[1].

3. RESULTS AND DISCUSSION

3-1. SYNTHESIS OF $La_2Co_{17-x-y}Fe_xM_y$

Figure 1 shows the X-ray diffraction patterns of La-(CoFe)-Mo alloys. Almost all the diffraction lines were fitted to Th_2Zn_{17}-type rhombohedral structure.
La-(Co, Fe)-M; (M=V, Mn, Nb, Ta, W) also have Th_2Zn_{17}-type rhombohedral structure, while the alloys with Cr, Zr and Hf don't form 2-17 compound.
Table 1 shows the lattice parameter obtained by fitting the diffraction lines to the Th_2Zn_{17}-type structure and magnetic properties of $La_2Co_{17-x-y}Fe_xM_y$.
This compound exists in the range of x=0-7 for M=Mn, Nb, Mo, Ta, W, and of x=0-5 for M=V. Beyond the threshold of x, 2-17 compound decomposes to 1-5 and 1-13.
On the other hand, $La_2Co_{17-x-y}Fe_xM_y$

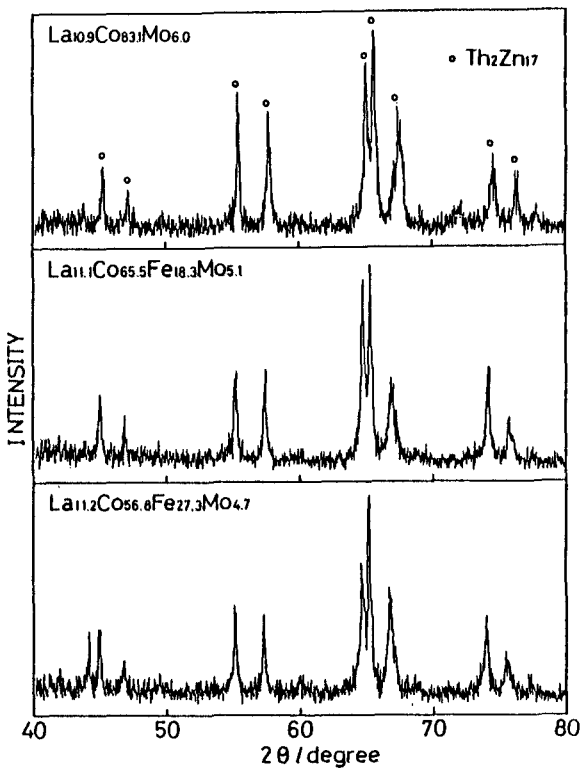

Fig.1 X-ray diffraction pattern of La-(CoFe)-Mo alloys.

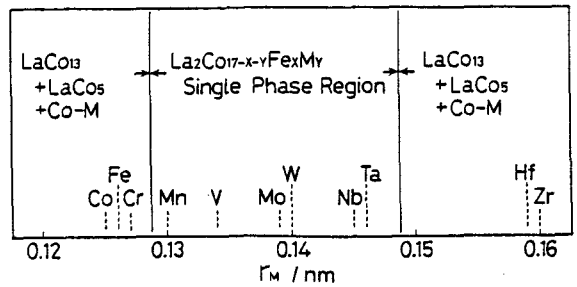

Fig.2 Stability region of comounds in atomic radius of additive elements, r_M.

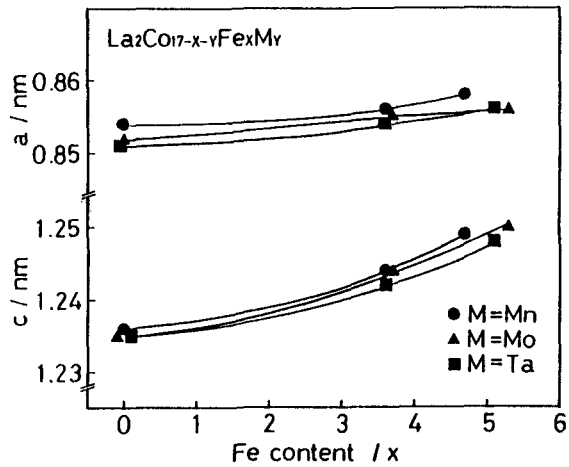

Fig.3 variation in lattice parameter with Fe content of $La_2Co_{17-x-y}Fe_xM_y$.

exists in the narrow range of M content, which depends on additive elements.

It is very interest to consider why 2-17 compound absent in La-Co binary system can be synthesized with the addition of specific elements.

In Ln-3d metal compounds, the crystal structure and lattice parameter have a regular dependences on the atom size of constituent excepting La and mixed valence Ln. Thus the formation of 2-17 compound can simply be governed by the size of atoms in a transition metal sublattice, since valence state of La is +3 like other Lanthanoids.

Figure 2 shows the stability region of compounds plotted against the atomic radius of additive elements, r_M.

$La_2Co_{17-x-y}Fe_xM_y$ exists in the region of r_M=0.130nm(Mn)-0.146nm(Ta). Therefore the atom size of additives is found to contribute to the formation of 2-17 compound in La-Co system. From the viewpoint of mean atom size effect, such as tolerance factor in ceramic materials[2] the lattice parameter and formation region of $La_2Co_{17-x-y}Fe_xM_y$ were tentatively correlated to the mean atomic radius of Co, Fe and M. But systematic correlation between them was not obtained.

Figure 3 shows the variation in the

Table 1 Structure and magnetic properties of $La_2Co_{17-x-v}Fe_xM_v$.

Compound	Structure type	a /nm	c /nm	J(1.5T) /T	$\mu_{F.U.}$ /μ_B	H_A /T	EDOM
$La_2Co_{16.3}V_{0.7}$	Th_2Zn_{17}	0.850	1.235	-	-	-	-
$La_2Co_{13.7}Fe_{2.6}V_{0.7}$	Th_2Zn_{17}	0.852	1.238	-	-	-	-
$La_2Co_{15.8}Mn_{1.2}$	Th_2Zn_{17}	0.854	1.236	1.09	24.3	1.9	c-axis
$La_2Co_{12.3}Fe_{3.6}Mn_{1.1}$	Th_2Zn_{17}	0.856	1.244	1.22	27.6	1.4	c-axis
$La_2Co_{11.0}Fe_{4.7}Mn_{1.3}$	Th_2Zn_{17}	0.858	1.249	(1.3)	-	1.2	c-axis
$La_2Co_{16.7}Nb_{0.3}$	Th_2Zn_{17}	0.852	1.236	0.98	21.8	-	-
$La_2Co_{13.7}Fe_{3.6}Nb_{0.2}$	Th_2Zn_{17}	0.854	1.242	1.26	28.3	-	c-plane
$La_2Co_{11.4}Fe_{5.3}Nb_{0.3}$	Th_2Zn_{17}	0.856	1.245	(1.04)	-	1.1	c-axis
$La_2Co_{16.2}Mo_{0.8}$	Th_2Zn_{17}	0.852	1.235	0.84	18.7	1.4	c-axis
$La_2Co_{12.7}Fe_{3.7}Mo_{0.6}$	Th_2Zn_{17}	0.855	1.244	1.12	25.2	-	c-plane
$La_2Co_{11.2}Fe_{5.3}Mo_{0.5}$	Th_2Zn_{17}	0.856	1.250	1.20	27.2	-	c-plane
$La_2Co_{16.7}Ta_{0.3}$	Th_2Zn_{17}	0.851	1.235	1.00	22.2	-	-
$La_2Co_{13.3}Fe_{3.6}Ta_{0.1}$	Th_2Zn_{17}	0.854	1.242	1.18	26.5	-	-
$La_2Co_{11.6}Fe_{5.1}Ta_{0.3}$	Th_2Zn_{17}	0.856	1.248	(1.18)	-	1.2	c-axis
$La_2Co_{16.5}W_{0.5}$	Th_2Zn_{17}	0.851	1.231	0.92	20.3	1.9	c-axis
$La_2Co_{16.7}Fe_{3.9}W_{0.4}$	Th_2Zn_{17}	0.853	1.242	1.17	26.2	-	-
$La_2Co_{11.4}Fe_{5.4}W_{0.2}$	Th_2Zn_{17}	-	-	-	-	-	-

EDOM: Easy direction for magnetization

lattice parameter with Fe content. The lattice parameter increases as Fe content increases and the maximun value of x for existence of 2-17 compound tends to increase slightly with increasing r_M. It is reported that Co sublattice sites in Ln_2Co_{17} is substituted by Fe atoms in order of Co(6c), Co(9d) or Co(18h) and Co(18j) in rhombohedral sturcture[3]. We reported that Fe atoms occupy preferably Co(6c) site in $La_2Co_{17-x-v}Fe_xTi_v$ and $La_2Co_{17-x-v}Fe_xTi_vN$ at x=3.3-6.7[1].

Therefore, Fe atoms occupy Co sites of $La_2Co_{17-x-v}Fe_xM_v$ in the similar order as well.

Cosequently, the formation of 2-17 compound in La-Co(Fe) system requires the addition of specific elements having r_M=0.130-0.146nm, but the concept of mean atom size effect is not valid for the condition of formation of 2-17 compound.

3.2. MAGNETIC PROPERTIES OF $La_2Co_{17-x-v}Fe_xM_v$

As shown in Table 1, J(1.5T) of $La_2Co_{17-x-v}Fe_xM_v$, which increases with an increase in Fe content, is from 0.84T to 1.26T. These values are relatively less than that of candidates for permanent magnets such as Sm_2Co_{17}, $Nd_2Fe_{14}B$ etc. Thus Magnetic moment per formula unit of $La_2Co_{17-x-v}Fe_xM_v$;(x=0) was calculated from the data of J(1.5T), and the magnetic moment of Co atom, μ_{Co} was estimated on the assumption that La and M

have no magnetic moment. μ_{Co} in these compounds is 1.15-1.30 μ_B for M=Nb,Mo,Ta W and 1.54 μ_B for M=Mn, which are far from μ_{Co} of pure Co, (1.70 μ_B).

μ_{Co} of Y_2Co_{17} is 1.63 μ_B little less than that of pure cobalt[4], so that the probability of electron transfer from Ln atoms to transition metal atoms may be low. Such a situation must occur in $La_2Co_{17-x-v}Fe_xM_v$. Thus low μ_{Co} must be caused by the electron transfer from additive metal atoms to Co atoms. On the other hand, relative high μ_{Co} for Mn samples can be referred to the low probability of electron transfer or anomaly of moment peculiar to Ln-3d metal- Mn system[4].

Magnetic anisotropy of $La_2Co_{17-x-v}Fe_xM_v$ must originate from an anisotropy of Co-Fe-M sublattice, because of the lack of 4f electron in La atom. Y_2Co_{17}, in which Y atoms also have no 4f electron , shows c-plane easy magnetization.

However, introduction of Fe to this compound brings about the c-axis easy magnetization, because Fe atoms substitute preferentially Co atoms in 6c site which has negative contribution to magnetic anisotropy[5]. Therefore, M atoms occupy 6c site in $La_2Co_{17-x-v}Fe_xM_v$;(M=Mn Mo,W), so that the contribution of 6c site to magnetic anisotropy is reduced and c-axis magnetization occurs.

Combining structural and magnetic approaches to $La_2Co_{17-x-v}Fe_xM_v$, it was deduced that the occupation of additive element atoms in 6c site induces the formation of 2-17 compound and c-axis magnetization. In other wards, the nature of 6c site is responsible to crystal structure and magnetic properties of $Ln_2(Co,Fe)_{17}$.

4. CONCLUSIONS

Through structural analyses and magnetic property measurements of La-Co-Fe-M alloys, it was found that Th_2Zn_{17}-type 2-17 compound was synthesized by the addition of transition elements having atomic radius of 0.130-0.146nm,(V,Mn,Nb, Ta,W). $La_2Co_{17-x-v}Fe_xM_v$ exists in narrow range of M content, while it has high solubility for Fe. The saturation magnetization of this compound is 0.84T-1.26T at room temperature, which increases with an increase in Fe content.

Easy direction for magnetization is c-axis for $La_2Co_{17-x-v}Fe_xM_v$;(M=Mn,Mo,W).

It was concluded that addtive elements occupy preferentially 6c site (dumbbell site), which contributes to formation of 2-17 compound and magnetic anisotropy.

5. REFERENCES

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