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Phase relation, crystal structure, and magnetic properties of La-Co-Si alloys

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The phase relation of the La-Co-Si ternary system in the La-poor region (≤ 25 at. % La) was determined by means of x-ray powder diffraction. In this region there exist four ternary compounds: $LaCoSi_3$, $LaCoSi_2$, $LaCo_2Si_2$, and $LaCo_{13-x}Si_x$. The cubic $LaCo_{13-x}Si_x$ intermetallic compound with $NaZn_{13}$-type structure could be changed to a tetragonal one with $NaZn_{13}$-derivative structure by vacuum annealing after arc melting. The tetragonal $LaCo_{13-x}Si_x$ compounds can exist stably in the composition range between $x=2.0$ and 5.0. The space group of the tetragonal $LaCo_{13-x}Si_x$ intermetallic compound is $I4/mcm$. The crystal structure of the tetragonal phase was refined by the Rietveld method. Si atoms show a strong preference for occupying a specific crystallographic position in the structure; i.e., atomic ordering occurs. Magnetic measurements indicate that the tetragonal $LaCo_{13-x}Si_x$ intermetallic compounds are ferromagnetic with Curie temperature higher than 900 K and anisotropy fields of about 10 kOe. The saturation magnetic moment per Co atom in the tetragonal $LaCo_{13-x}Si_x$ compounds decreases with Si content. The composition dependence of the saturation magnetic moment per Co atom can be satisfactorily explained by the rigid-band model.

I. INTRODUCTION

Since the discovery of the excellent permanent magnetic material $Nd_2Fe_{14}B$,[1,2] a worldwide search for other materials has been carried out. It is believed that there exist other compounds in the still unexploited reservoir of ternary compounds containing rare-earth element R and transition metal.[3] The emergence of $RFe_{12-x}M_x$ (M=Ti, V, Cr, Mo, W, or Si) compounds with $ThMn_{12}$-type structure[4] and $R_2Fe_{17}M_x$ (M=C or N) compounds with Th_2Zn_{17}- or Th_2Ni_{17}-type structure[5,6] as promising candidates for permanent magnets encourages the exploitation of magnetic materials in the R-T-M system.

$LaCo_{13}$ compound has a large magnetization and a high Curie temperature, $4\pi M_s = 13$ kG and $T_c = 1318$ K, because its $3d$ metal content is the highest among all rare-earth transition-metal intermetallic compounds.[7] Moreover, among all binary rare-earth Fe, Co, or Ni systems, only in the La-Co system does an intermetallic compound with $NaZn_{13}$-type structure exist stably. By substituting Al or Si for part of the transition metal, the $NaZn_{13}$-type structure can be stabilized in other binary rare-earth–transition-metal systems.[8–11] The substitution of other rare-earth elements for La in $LaCo_{13-x}Fe_x$ was found to be very limited.[11] However, although the $LaCo_{13}$-based intermetallic compounds with $NaZn_{13}$-type structure have large magnetizations and high Curie temperatures, they possess a cubic symmetry and lack significant magnetocrystalline anisotropy. Hence the $LaCo_{13}$-based intermetallic compounds with $NaZn_{13}$-type structure cannot be used for permanent magnets. Much larger magnetic anisotropy is expected in materials with a strongly anisotropic crystal structure (hexagonal or tetragonal symmetry, for instance). Unfortunately, Huang *et al.* recently failed to lower the symmetry of $LaCo_{13-x}Fe_x$ compounds by nitrogenation.[12]

The space group of the crystal structure of $LaCo_{13}$ compound is $Fm3c$. In this structure, Co atoms occupy two different crystallographically equivalent positions: $8(b)$ and $96(i)$, which are denoted as Co I and Co II, respectively, and La atoms and Co I atoms form a simple CsCl-type structure. Each La atom has 24 nearest neighbors of Co II atoms located at the corners of a "snub cube," and each Co I atom is surrounded by an icosahedron of 12 Co II atoms.[9,13] When part of the Co atoms in the $LaCo_{13}$ compound are substituted by other atoms such as Al, Si, etc., there exists the possibility that the substituting atoms occupy some specific positions in the structure, especially when Co II atoms are substituted. In other words, ordered substitution would occur. In this case, the symmetry of the crystal structure would degrade from a cubic symmetry to a lower symmetry (tetragonal or orthorhombic). The original motivation

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for our present and other works[14,15] is to realize such a symmetry reduction.

Furthermore, the phase relations of *R*-*T*-*M* systems are usually very similar because of the similarity of the chemical and physical properties of rare-earth metals. The phase relation of the La-Co-*M* system, however, will appear as an exception, since the intermetallic compound with $NaZn_{13}$-type structure can only exist stably in the La-Co binary system among all *R*-*T* (T=Fe, Co, or Ni) binary systems, and the existence of $LaCo_{13}$ compound suppresses the occurrence of the intermetallic compound with Th_2Zn_{17}- or Th_2Ni_{17}-type structure usually found in other *R*-*T* binary systems. Therefore, the study on the phase relationship of the La-Co-*M* system will play a unique role in the systematic study on the phase relations of *R*-*T*-*M* ternary systems, which is of significance for fundamental research and practical application of the materials.

In this paper, we will first report in Sec. III our experimental results of the phase relation of the La-Co-Si system in the La-poor region ($\leq$25 at. % La), and then present preliminary Rietveld refinement results of the crystal structures of the tetragonal $LaCo_{13-x}Si_x$ intermetallic compounds in Sec. IV. Magnetic properties of the tetragonal $LaCo_{13-x}Si_x$ compounds will be reported in Sec. V, and explained by the rigid-band model. Finally, brief discussions and conclusions will be given in Sec. VI.

II. EXPERIMENTAL PROCEDURES

Alloys were prepared by arc melting the appropriate amount of the starting materials in an atmosphere of ultrapure argon gas. The purity of the starting materials was better than 99.9%. The weight loss of the samples during arc melting was less than 1%. After arc melting, all the samples were vacuum annealed at 1273 K for one month and analyzed by x-ray diffraction. Afterwards, all the samples were further vacuum annealed at 873 K for three months. No noticeable change of weight of the samples was observed after annealing.

The phase identification of the samples was carried out by x-ray powder diffraction, using a four-layer monochromatic focusing Guinier–de Wolff camera with FeKα radiation. High-purity Si powder was used as an inner standard for measurement of the lattice parameters. The diffraction intensity data were collected by a MXP18A-HF diffractometer with rotating anode, which had an 18 kW x-ray generator and CuKα radiation. A graphite monochromator was used for diffracted beams. A step-scan mode was adopted with a scanning step of 0.02° and a sampling time of 2 sec.

The composition dependences of the Curie temperature and magnetization of the $LaCo_{13-x}Si_x$ bulk samples were determined by Faraday balance and extracting sample magnetometer measurements, respectively. The magnetizations of a field aligned powder sample was measured by a superconducting quantum interference device (SQUID) magnetometer. The fine powders (<15 μm) were oriented in a field of about 10 kOe and fixed in epoxy resin to form a cylindrical specimen with $\phi=5$ mm in diameter and $h=5$ mm in height. The orienting field was along the cylindrical axis. For all magnetic measurements, the self-demagnetizing effects were taken into account by adopting $N=4\pi/3$ as a demagnetizing factor.

III. PHASE RELATION OF La-Co-Si TERNARY SYSTEM IN La-POOR REGION

Two sets of samples were prepared. One was along the line with constant La content of about 7 at. %, i.e., $LaCo_{13-x}Si_x$ ($0\leq x\leq 10$), and the other was distributed on both sides of the line. The nominal compositions and x-ray diffraction (XRD) identified phases in the samples annealed at 873 K are shown in Table I.

For as-cast $LaCo_{13-x}Si_x$ samples, x-ray-diffraction patterns indicated that single phase samples with the cubic $NaZn_{13}$-type structure were obtained in the concentration range between $x=0$ and 2.5, which agrees with the reported results of Palstra *et al.*[10] A tetragonal phase coexisting with minor Co_2Si was found in the samples with $x=3.0-5.0$. Three phases: $LaCo_2Si_2$, CoSi, and

TABLE I. Composition and XRD identified phases in La-Co-Si alloys annealed at 873 K.

Composition	Phases[a]	Composition	Phases[a]
$LaCo_{13}$	1:13(*C*)	$LaCo_5Si_8$	CoSi,$CoSi_2$,$LaCoSi_3$
$LaCo_{12.5}Si_{0.5}$	1:13(*C*)	$LaCo_3Si_{10}$	$CoSi_2$,$LaCoSi_3$,Si
$LaCo_{12.0}Si_{1.0}$	1:13(*C*)	$LaCoSi_2$	$LaCoSi_2$
$LaCo_{11.5}Si_{1.5}$	1:13(*C*)	$La_{0.18}Co_{0.79}Si_{0.03}$	$LaCo_5$,La_2Co_7,1:13(*C*)
$LaCo_{11.0}Si_{2.0}$	1:13(*T*),Co[b]	$La_{0.16}Co_{0.64}Si_{0.20}$	La_2Co_7,$LaCo_2Si_2$,1:13(*T*)
$LaCo_{10.5}Si_{2.5}$	1:13(*T*),Co[b]	$La_{0.16}Co_{0.38}Si_{0.46}$	$LaCoSi_2$,$LaCo_2Si_2$CoSi
$LaCo_{10.0}Si_{3.0}$	1:13(*T*),Co[b]	$La_{0.13}Co_{0.84}Si_{0.03}$	$LaCo_5$, 1:13(*C*)
$LaCo_{9.5}Si_{3.5}$	1:13(*T*),Co_2Si[b]	$La_{0.10}Co_{0.84}Si_{0.06}$	1:13(*C*)
$LaCo_{9.0}Si_{4.0}$	1:13(*T*),Co_2Si[b]	$La_{0.10}Co_{0.77}Si_{0.13}$	1:13(*T*)
$LaCo_{8.5}Si_{4.5}$	1:13(*T*),Co_2Si[b]	$La_{0.10}Co_{0.59}Si_{0.31}$	$LaCo_2Si_2$, 1:13(*T*)
$LaCo_{8.25}Si_{4.75}$	1:13(*T*),Co_2Si[b]	$La_{0.05}Co_{0.82}Si_{0.13}$	Co,1:13(*T*)
$LaCo_{8.0}Si_{5.0}$	1:13(*T*),Co_2Si[b]	$La_{0.05}Co_{0.64}Si_{0.31}$	Co_2Si,1:13(*T*)
$LaCo_{7.5}Si_{5.5}$	1:13(*T*),$LaCo_2Si_2$,CoSi	$La_{0.05}Co_{0.55}Si_{0.40}$	CoSi,1:13(*T*)
$LaCo_{7.0}Si_{6.0}$	1:13(*T*),$LaCo_2Si_2$,CoSi	$La_{0.03}Co_{0.74}Si_{0.23}$	Co_2Si,Co,1:13(*T*)
$LaCo_{6.0}Si_{7.0}$	CoSi,$LaCoSi_2$,$LaCoSi_3$	$La_{0.03}Co_{0.58}Si_{0.38}$	Co_2Si,CoSi,1:13(*T*)

[a] 1:13(*C*)=cubic $NaZn_{13}$-type structure; 1:13(*T*)=tetragonal $NaZn_{13}$-derivative structure.

[b] Minor phase.

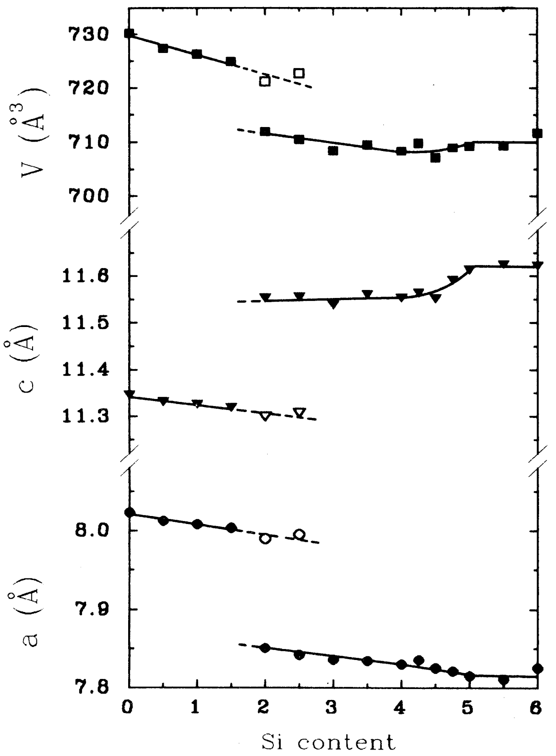

FIG. 1. The concentration dependences of lattice parameters of the tetragonal $LaCo_{13-x}Si_x$ compounds annealed at 873 K. For samples having the cubic $NaZn_{13}$-type structure, $a=a_c/\sqrt{2}$, $c=a_c$, and $V=V_c/2$ are plotted. The data for as-cast $LaCo_{11}Si_2$ and $LaCo_{10.5}Si_{2.5}$ with the $NaZn_{13}$-type structure are shown by the corresponding hollow symbols.

the tetragonal phase, coexisted in the samples with $x=5.5$ and 6.0. When $x \geq 7.0$, the tetragonal phase disappeared completely in the samples.

After vacuum annealing the $LaCo_{13-x}Si_x$ samples at 1273 K for one month, the x-ray-diffraction patterns showed that the phases existing in the samples did not change except for those with $x=2.0$ and 2.5. As-cast $LaCo_{11}Si_2$ and $LaCo_{10.5}Si_{2.5}$ compounds had the cubic $NaZn_{13}$-type structure with $a=11.299(2)$ and 11.307(3) Å, respectively. After the annealing treatment, splitting of the diffraction peaks occurred, and a small amount of Co segregated. Further vacuum annealing at 873 K for three months resulted in a more obvious and sharp splitting of the diffraction peaks. The refinement of the structure indicates that the amount of Co is less than 5 wt. % (see Sec. IV). The diffraction patterns of the annealed $LaCo_{11}Si_2$ and $LaCO_{10.5}Si_{2.5}$ compounds are the same as those of other $LaCo_{13-x}Si_x$ compounds with $x>2.5$, and were successfully indexed with a tetragonal lattice.[15]

Figure 1 shows the concentration dependences of the lattice parameters of $LaCo_{13-x}Si_x$ compounds annealed at 873 K. It is evident from Fig. 1 that the homogeneous range of the cubic $LaCo_{13-x}Si_x$ compound is smaller than $x=2.0$. Between $x=1.5$ and 2.0 there is a phase transition from a cubic symmetrical structure to a tetragonal symmetrical structure. The discontinuity of the lattice parameters implies that the phase transition should be a first-order transition. The lattice parameters of as-cast $LaCo_{11}Si_2$ and $LaCo_{10.5}Si_{2.5}$ compounds with cubic $NaZn_{13}$ structure are also shown in Fig. 1, and they coincide well with the extrapolation of the data of $x \leq 1.5$. The lattice parameters of the tetragonal $LaCo_{13-x}Si_x$ compound change linearly with Si content up to $x=4.0$, and monotonically at higher values. Such a concentration dependence of the lattice parameters of the tetragonal $LaCo_{13-x}Si_x$ compound might be attributed to the magnetic disordering and preferred occupation of Si atoms in the structure (see Sec. VI). Therefore, the homogeneous range of the tetragonal $LaCo_{13-x}Si_x$ compound is between $x=2.0$ and 5.0.

Based on the data in Table I and Fig. 1, the phase relation of the La-Co-Si ternary system in the La-poor region is constructed (Fig. 2).

IV. CRYSTAL STRUCTURE OF THE TETRAGONAL $LaCo_{13-x}Si_x$ COMPOUND

The x-ray-diffraction pattern of $LaCo_{13-x}Si_x$ ($2.0 \leq x \leq 5.0$) intermetallic compounds annealed at 873 K were successfully indexed with a tetragonal lattice us-

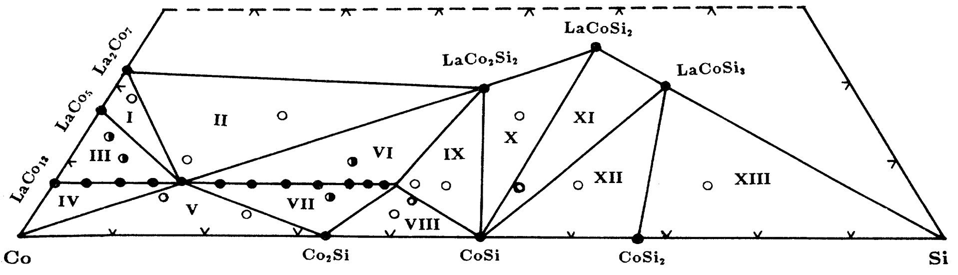

FIG. 2. The phase relation of the La-Co-Si ternary system at 873 K. ●: single phase; ◑: two phases; ○: three phases;

I: $LaCo_5+La_2Co_7+1{:}13(C)$;
II: $La_2Co_7+LaCo_2Si_2+1{:}13(T)$;
III: $LaCo_5+1{:}13(C)$;
IV: $Co+1{:}13(C)$;
V: $Co+Co_2Si+1{:}13(T)$;
VI: $LaCo_2Si_2+1{:}13(T)$;
VII: $Co_2Si+1{:}13(T)$;
VIII: $Co_2Si+CoSi+1{:}13(T)$;
IX: $CoSi+LaCo_2Si_2+1{:}13(T)$;
X: $CoSi+LaCo_2Si_2+LaCoSi_2$;
XI: $CoSi+LaCoSi_2+LaCoSi_3$;
XII: $CoSi+CoSi_2+LaCoSi_3$;
XIII: $Si+CoSi_2+LaCoSi_3$.

TABLE II. Rietveld refinement results for the atomic positions in a unit cell of the tetragonal $LaCo_{13-x}Si_x$ compounds.

Atom	Position	x/a	y/b	z/c	x
4 La	4(*a*)	0.0	0.0	0.25	2.5,3.5,4.75
4 Co	4(*d*)	0.0	0.5	0.0	2.5,3.5,4.75
		0.1235(5)	0.6235(5)	0.1828(4)	2.5
16 Co	16(*l*)	0.1240(6)	0.6240(6)	0.1937(3)	3.5
		0.1291(3)	0.6291(3)	0.1801(3)	4.75
16 Co		0.2089(6)	0.0754(6)	0.0	2.5
16 Co	16(*k*)	0.2125(7)	0.0564(11)	0.0	3.5
13 Co+3 Si		0.1993(5)	0.0692(6)	0.0	4.75
6 Co+10 Si		0.3415(6)	0.8415(6)	0.1373(8)	2.5
2 Co+14 Si	16(*l*)*	0.3658(12)	0.8658(12)	0.1352(10)	3.5
16 Si		0.3324(7)	0.8324(7)	0.1253(7)	4.75

ing the program TREOR,[16] and the lattice parameters were further least-square refined by the program PIRUM. The lattice parameters were determined to be $a = 7.850 - 7.815(3)$ Å and $c = 11.552 - 11.616(7)$ Å. The space group was derived to be $I4/mcm$ based on the reflection conditions: hkl: $h+k+l=2n$; $0kl$: $l=2n$, and $h0l$: $l=2n$. The ratio of lattice parameters c and a is approximately equal to $\sqrt{2}$, which implies that the tetragonal structure of $LaCo_{13-x}Si_x$ compound is a $NaZn_{13}$ derivative structure. The number of chemical formula per unit cell of the tetragonal structure is 4. Preliminary refinements of the tetragonal structure have been performed by the Rietveld method[17] for $LaCo_{10.5}Si_{2.5}$, $LaCo_{9.5}Si_{3.5}$, and $LaCo_{8.25}Si_{4.75}$ compounds. The refinement results are shown in Table II and Fig. 3. The weighted pattern R factors,[18] R_{wp}, are 8.75%, 14.97%, and 14.91% for $LaCo_{10.5}Si_{2.5}$, $LaCo_{9.5}Si_{3.5}$, and $LaCo_{8.25}Si_{4.75}$, respectively. The amounts of impurity

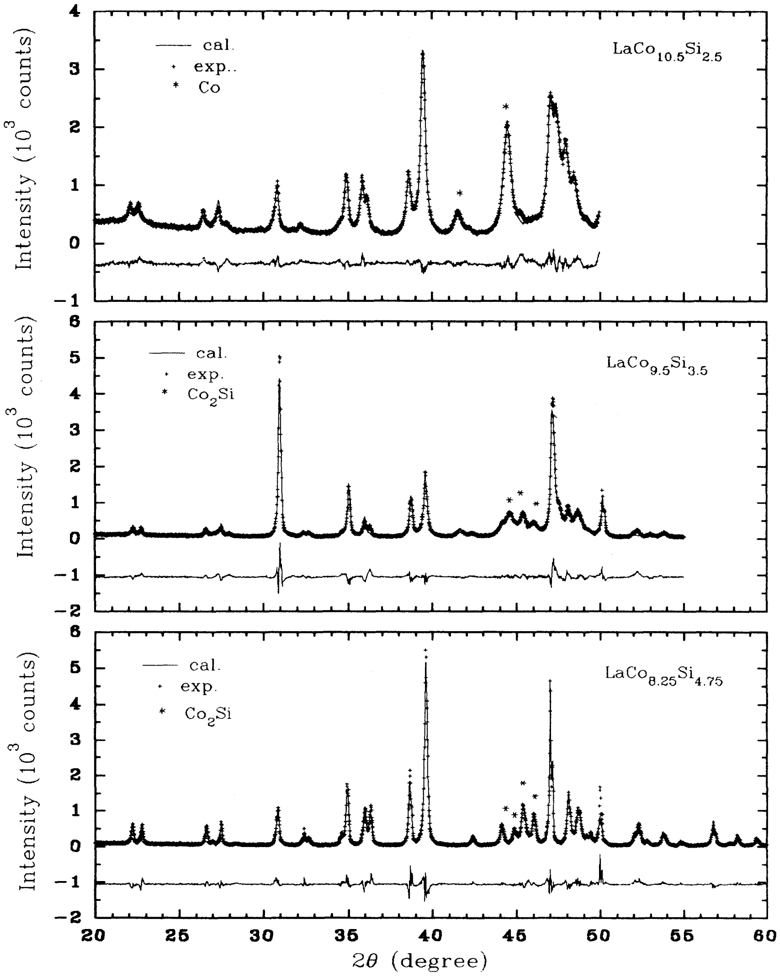

FIG. 3. Output from Rietveld analysis of the XRD pattern. The observed data are indicated by crosses and the calculated profile is the continuous line overlaying them. The lower curve is the difference between the observed and calculated intensity at each step, plotted on the same scale and shifted a little downwards for clarity.

phases existing in the samples were estimated from Rietveld refinement results[19] to be less than 5 wt. % in $LaCo_{10.5}Si_{2.5}$, and less than 8 wt. % in $LaCo_{9.5}Si_{3.5}$ and $LaCo_{8.25}Si_{4.75}$. The occurrence of the impurity phases was probably due to some loss of La atoms because of the oxidation of La atoms enriched on the surface.[20] The magnetic measurements also indicated that the amount of the impurity phases was very small.[15] The apparent strong Co peaks in Fig. 3 are probably due to the high symmetry of the crystal structure of Co.

The Rietveld refinement of the crystal structure of the tetragonal $LaCo_{13-x}Si_x$ compounds reveals that Si atoms show a strong preference for occupying the $16(l)^*$ position with $x/a \simeq 0.34$ and $z/c \simeq 0.13$. In other words, atomic ordering occurs in the $LaCo_{13-x}Si_x$ $(2.0 \leq x \leq 5.0)$ compounds after annealing, and the crystal structure does change from cubic to tetragonal. The lowering of the structural symmetry could be easily observed in the XRD patterns.[15] The illustration of the crystal structure of the tetragonal $LaCo_{8.25}Si_{4.75}$ compound, together with the coordination polyhedra of a La atom in the $4(a)$ site and a Co atom in the $4(d)$ site are shown in Fig. 4. The shape of the coordination polyhedra of La atom and Co atom in $4(d)$ is similar to that in the cubic $LaCo_{13}$ structure except for the atomic ordering of the atoms at the corners of the polyhedra, which results in some distortion.

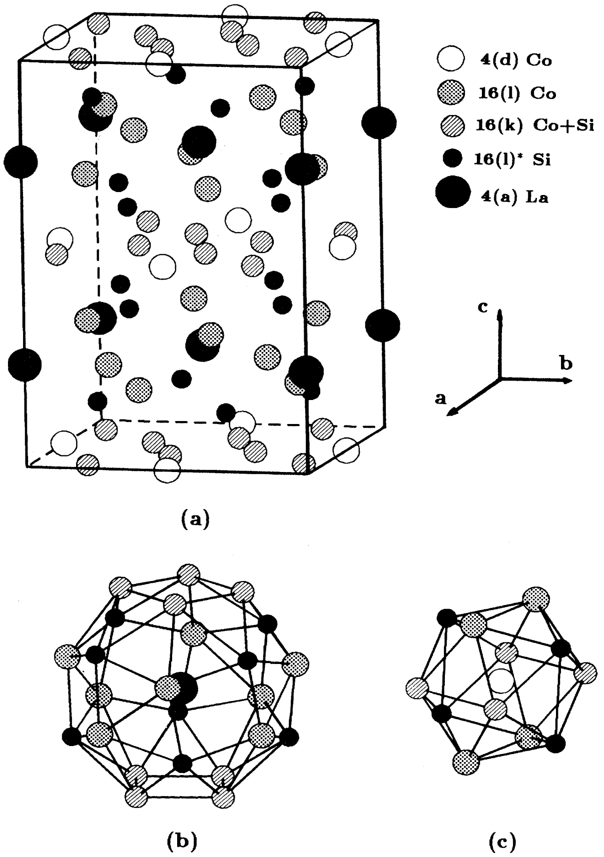

FIG. 4. Illustration of (a) the structure of $LaCo_{8.25}Si_{4.75}$ compound, (b) coordination polyhedrons of a La atom, and (c) a Co atom.

A problem would arise when $x > 4.0$, where the $16(l)^*$ position has been completely occupied by Si atoms. There are three different crystallographic equivalent positions in the structure for the excess Si atoms to take: $4(d)$, $16(l)$ $(x/a \simeq 0.12,\ z/c \simeq 0.19)$, and $16(k)$. Focusing on the R factor, the quality of the refinement, during the structure refinement for the $LaCo_{8.25}Si_{4.75}$ compound, we observed that the excess Si atoms show a preference for occupying the $16(k)$ position. The R factor became obviously higher when excess Si atoms occupied the $4(d)$ or $16(l)$ positions. In particular, if occupancy in the $4(d)$ position was included in the refinement, the R factor did decrease a little along with the result that the $4(d)$ position was almost fully occupied by Co atoms. This result implies that the $Ce_2Ni_{17}Si_9$-type structure[21] is excluded for $LaCo_{13-x}Si_x$ compounds. The conclusion is consistent with the neutron-scattering measurement on $LaFe_{13-x}Al_x$ compounds with $NaZn_{13}$-type structure.[22] It was shown that Al atoms avoided the $8(b)$ position in the cubic structure. The $8(b)$ position in the cubic structure is transformed into the $4(d)$ position in the $NaZn_{13}$ derivative structure. From the viewpoint of structural chemistry, since the Si atoms have already been distributed on four of the six quadrangles of the coordination polyhedron, a "snub cube," of La atoms [Fig. 4(b)], the excess Si atoms are most likely distributed on the other two quadrangles. If further atomic ordering occurs in the $16(k)$ position, the structure would change to an orthogonal one as was observed in $LaFe_7Al_6$ and $LaFe_6Al_7$ compounds.[14]

V. MAGNETIC PROPERTIES OF THE TETRAGONAL $LaCo_{13-x}Si_x$ COMPOUNDS

Some of the magnetic properties of the tetragonal $LaCo_{13-x}Si_x$ compounds have been reported previously.[15] Magnetic balance measurements in a magnetic field of 12 kOe indicated that the tetragonal $LaCo_{13-x}Si_x$ compounds were ferromagnetic with Curie temperatures higher than 900 K in the composition range between $x=2.0$ and 4.0. The Curie temperatures of the tetragonal $LaCo_{13-x}Si_x$ compounds decrease linearly with Si content. The saturation magnetic moment per Co atom decreases monotonically with Si content and could be satisfactorily explained by the rigid-band model, i.e.,

$$\mu_{Co}(x)=(10-n_0)-Nx/(13-x)\ , \tag{1}$$

with $n_0=8.07$ and $N=4$. We suggested that the Co $3d$ band with up-spin in the tetragonal $LaCo_{13-x}Si_x$ compounds has been filled when $x \geq 2.0$.[15]

Figure 5 shows the field dependences of magnetization of the $LaCo_{13-x}Si_x$ compounds measured by an extracting sample magnetometer at 77 K in a field up to 65 kOe. It is evident that the cubic $LaCo_{13-x}Si_x$ $(x=1.5)$ is much easier to magnetize to its saturation state than the tetragonal $LaCo_{13-x}Si_x$ $(x=2.0-4.0)$. Since the area enclosed by the magnetization curve, the vertical axis and the line $M=M_s$, where M_s is the saturation magnetiza-

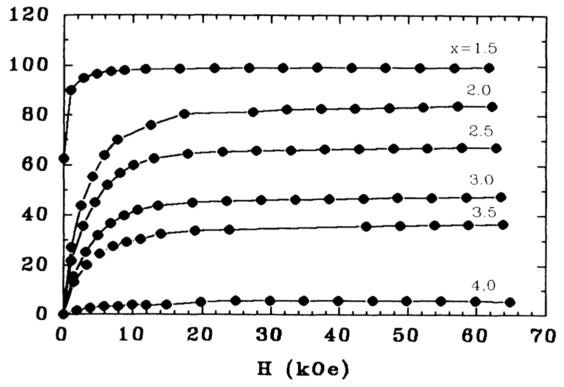

FIG. 5. Field dependences of magnetization of the $LaCo_{13-x}Si_x$ compounds at 77 K.

tion, represents the energy required to magnetize a unit volume of the specimen to its saturation state,[23] it could be inferred that the anisotropy field in the tetragonal $LaCo_{13-x}Si_x$ is larger than that in cubic $LaCo_{13-x}Si_x$ as expected. In principle, the anisotropy field of a magnetic compound can be derived from the magnetization curve based on the law of approach to saturation, but in this method small errors in the measurement of M may have a fatal influence on the determination of the anisotropy field.[23] Another approach to estimate the anisotropy field is based on the singular-point detection technique (SPD),[24,25] in which the magnetization curve $M(H)$ of a polycrystalline ferromagnet has a singularity located at the anisotropy field H_A and the singularity appears in a particular derivative of the magnetization, d^nM/dH^n, at H_A. By numerically analyzing the magnetization curves shown in Fig. 5, the anisotropy fields in the tetragonal $LaCo_{13-x}Si_x$ are estimated to be about 10–12 kOe at 77 K.

Figure 6 shows the magnetization curve of field aligned powder of tetragonal $LaCo_{10}Si_3$ compound measured at 35 K by a SQUID magnetometer along and perpendicular to the orientation direction. The anisotropy field is estimated to be about 12 kOe, which is in excellent agreement with the SPD analysis of the magnetization curve shown in Fig. 5 and comparable to the anisotropy fields in other R-T-M ternary compounds with R = La, Y, and Lu.[3,4]

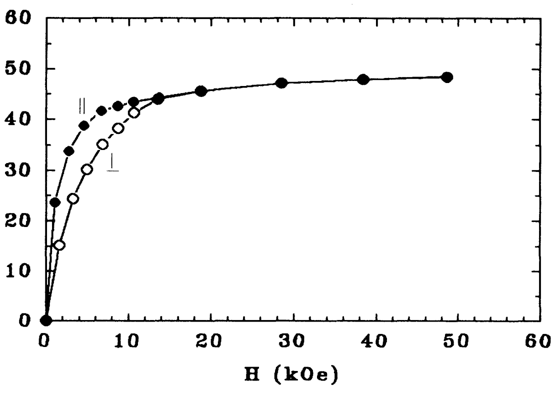

FIG. 6. Field dependences of the magnetization of the tetragonal $LaCo_{10}Si_3$ compound measured at 35 K along and perpendicular to the orientation direction.

It is worth noting that the magnetism of $LaCo_{13-x}Si_x$ is solely attributed to the Co sublattice within the framework of the two-sublattice mean-field approximation,[3] in which La atoms are supposed to be nonmagnetic. Magnetic rare-earth atoms with $4f$ electrons usually contribute large magnetocrystalline anisotropy due to the effect of crystalline electric fields on the $4f$-electron wave functions. Weitzer *et al.* reported that the substitution of magnetic rare-earth metals for La did increase the magnetocrystalline anisotropy of $LaCo_{13-x}Ga_x$ compounds with tetragonal symmetry.[26]

VI. DISCUSSIONS AND CONCLUSIONS

According to the structural model we present for the tetragonal $LaCo_{13-x}Si_x$ compounds, Si atoms will preferentially occupy the $16(l)^*$ position when $x \leq 4.0$, and the excess Si atoms will take the $16(k)$ position when $x > 4.0$. As shown in Fig. 4, the atoms in the $16(k)$ and $4(d)$ positions form an atom plane at $c/z = 0$, which has two nearest Si atom planes at $c/z \simeq \pm 0.13$. When the excess Si atoms occupy the $16(k)$ position, the Si atom planes at $c/z \simeq \pm 0.13$ would be repelled and this may be the reason for the increase of lattice parameters c and volume V of the tetragonal $LaCo_{13-x}Si_x$ compounds with $x > 4.0$. In this case, obvious increases of c and V should start at $x = 4.0$ instead of at $x = 4.5$ as shown in Fig. 1. It is plausible that the slower changes of c and V between $x = 4.0$ and 4.5 are due to the magnetic disordering. Magnetic ordering introduces stress in the crystal lattice and generally causes lattice parameters to change as a function of composition or temperature. For instance, the lattice parameters a and V of iron decrease a little on passing through the Curie point (1043 K).[27] It can be easily derived from Eq. (1) that μ_{Co} vanishes at $x = 4.23$. Therefore, the resultant effect of the magnetic disordering and the occupation of the $16(k)$ position by the excess Si atoms might result in the slower changes of the lattice parameters of $LaCo_{13-x}Si_x$ in the composition range between $x = 4.0$ and 4.5.

The present structure model for the tetragonal $LaCo_{13-x}Si_x$ compounds suggests that the homogeneous range of the compound would be greater than $x = 5.0$. However, there exists a large coordination number of atoms in the structure. The stability of the structure with a large coordination number of atoms is usually sensitive to the ratio of the atomic radii of the constitutes[27,28] and the volume fraction at close packing.[29,30] Therefore, the change of the average ratio of atomic radii and the increase of the unit-cell volume with Si content would prohibit the homogeneous range of the tetragonal $LaCo_{13-x}Si_x$ compounds from extending beyond $x = 5.0$.

Furthermore, the Rietveld refinement of the structure indicates a strong preferred orientation along the ⟨001⟩ direction in the powder sample as shown in Fig. 3 for the $LaCo_{9.5}Si_{3.5}$ compound. The preferred orientation was introduced during the preparation of the specimen for the diffractometer, and can be easily understood by the arrangement of the atoms in the structure (Fig. 4). The structure can be viewed as consisting of atom planes stacking along the ⟨001⟩ direction. Therefore, (001) planes will be easily exposed when the sample is crushed.

In conclusion, a cubic $LaCo_{13-x}Si_x$ compound can be changed into a tetragonal $LaCo_{13-x}Si_x$ compound by suitable annealing after arc melting. The space group of the tetragonal structure is $I4/mcm$. Atomic ordering takes place in the tetragonal $LaCo_{13-x}Si_x$ compounds, i.e., Si atoms show a strong preference for occupying a specific crystallographic position. The tetragonal $LaCo_{13-x}Si_x$ $(2.0 \leq x \leq 4.0)$ compounds are ferromagnetic with Curie temperatures higher than 900 K. The saturation magnetic moment of the tetragonal $LaCo_{13-x}Si_x$ compounds is large, and comparable to that of cubic $LaCo_{13-x}Si_x$ compounds. The anisotropy fields of the tetragonal $LaCo_{13-x}Si_x$ are about 10–12 kOe and are expected to increase with the substitution of La by magnetic rare-earth metals. It is believed that a similar phenomenon, i.e., atomic ordering and lowering of the crystal symmetry, can take place in other (R_1,R_2) $(Fe,Co)_{13-x}M_x$ compounds. Such a systematic investigation is under way in our laboratory.

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