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Magnetic properties of $Ln_{2.1}Co_{16.9}Si$ alloys

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Following up a study of stoichiometric compounds $Ln_2Co_{16}Si$, we report here magnetic properties of off-stoichiometric $Ln_{2.1}Co_{16.9}Si$ alloys, where Ln = La, Ce, Pr, Sm, and Gd. All the investigated compounds were found to crystallize with the rhombohedral Th_2Zn_{17} type, except the off-stoichiometric Ce compound, which, contrary to the $Ce_2Co_{16}Si$ alloy, was found to adopt the hexagonal Th_2Ni_{17} type under the experimental conditions. The magnetic properties of polycrystalline samples were investigated in the temperature range 1.9-1100 K in various magnetic fields. The field dependence of the magnetization was studied at T = 1.9 and 4.2 K. As for the stoichiometric compounds, saturation was observed in relatively low magnetic fields. The temperature dependence of the magnetization was measured in a field of 50 Oe between 1.9 and 400 K, and in a magnetic field of 4.83 kOe in the temperature range 300-1100 K. The Curie points of the off-stoichiometric compounds are below 1000 K and do thus not reach those of their stoichiometric homologues. The highest value was observed for the La alloy, indicating competition between the magnetic moments of the Co and lanthanide sublattices.

Ternary rare-earth silicides / Magnetic properties / Magnetic phase transition / High-magnetic field measurements

Introduction

Rare-earth (Ln) transition metal (T) compounds of the 2:17 type, with T = Fe or Co, have attracted much attention during the past few decades because of their promising magnetic properties and potential applications as materials for hydrogen storage. The magnetocrystalline anisotropy of these compounds is of substantial technological and theoretical interest. A strong uniaxial magnetic anisotropy is required to achieve high coercivity, however, the Ln_2Co_{17} binary compounds exhibit uniaxial anisotropy only for Ln = Sm, Er, and Tm. The structures and magnetic properties of $Ln_2Co_{17-x}Si_x$ alloys, where Ln = Y, Ce, Pr, Nd, Gd, Ho, and Dy, have been investigated recently [1-9]. The binary compounds have the hexagonal Th_2Ni_{17} structure when Ln = Y, Ce, or Ho [1,2,6,7], whereas the rhombohedral Th_2Zn_{17} structure is observed when Ln = Pr, Nd, Gd, or Dy [3-5,8]. The same structures are exhibited by $Ln_2Co_{17-x}Si_x$ pseudobinaries [1-8]. In some cases, for higher Si concentrations both structure types coexist (see e.g. [1,2,8]). Lately, it has been found that the substitution of Si for Co does not increase the Curie temperature, but for selected rare-earth elements it causes a change in the easy magnetization direction (EMD) from the basal plane to the *c*-axis [1,2,6]. However, for Ln = Gd, this transformation appears only at high temperature [5]. As a rule, the Co moment and the Curie temperature decrease with increasing Si concentration [1-9]. Such a regularity is not observed for alloys with Fe as the transition metal (see e.g. [10,11]). Recently, band structure calculations have been performed on Ln_2Co_{17} compounds, where Ln is a heavy rare earth or yttrium by using the TB-LMTO-ASA method [12]. They allow us to conclude that both local 4*f*–5*d* and 5*d*–3*d* short-range interactions contribute to the 5*d* band polarization, however, they do not provide a clear indication concerning how to improve the magnetic properties.

Only recently it has been established that $Ln_2Co_{17-x}Si_x$ alloys exist in a broader composition

Table 1 Crystallographic data for $Ln_2Co_{16}Si$ and $Ln_{2.1}Co_{16.9}Si$ alloys.

Alloy	Structure type	*a* [nm]	*c* [nm]	Ref.
$Y_2Co_{16}Si$	Th_2Zn_{17}	0.8342	1.2195	[1]
$La_{2.1}Co_{16.9}Si$	Th_2Zn_{17}	0.8411(2)	1.2234(4)	this work
$Ce_2Co_{16}Si$	Th_2Zn_{17}	0.8348	1.2192	[2]
$Ce_{2.1}Co_{16.9}Si$	Th_2Ni_{17}	0.8346(2)	0.8150(3)	this work
$Pr_2Co_{16}Si$	Th_2Zn_{17}	0.8439	1.2245	[3]
$Pr_{2.1}Co_{16.9}Si$	Th_2Zn_{17}	0.8415(2)	1.2240(4)	this work
$Nd_2Co_{16}Si$	Th_2Zn_{17}	0.8417	1.2257	[4]
$Sm_{2.1}Co_{16.9}Si$	Th_2Zn_{17}	0.8360(2)	1.2230(5)	this work
$Gd_2Co_{16}Si$	Th_2Zn_{17}	0.8369	1.2216	[5]
$Gd_{2.1}Co_{16.9}Si$	Th_2Zn_{17}	0.8338(2)	1.2213(5)	this work
$Tb_{2.1}Co_{16.9}Si$	Th_2Ni_{17}	0.83196(7)	0.81033(7)	[9]
$Dy_2Co_{16}Si$	Th_2Zn_{17}	0.8416	1.2155	[8]
$Ho_2Co_{16}Si$	Th_2Zn_{17}	0.8330	1.2176	[6]

range [9,13] and, therefore, we are now extending our research to the pseudobinary $Ln_{2.1}Co_{16.9}Si$ alloys, where Ln = La, Ce, Pr, Sm, and Gd.

Experimental

The alloys were prepared by melting the components in proportions corresponding to the final compositions in an arc furnace under an argon atmosphere, and were annealed at 900°C in vacuum for 1 week. X-ray diagrams were recorded at HZG-4a and DRON-2.0 diffractometers at room temperature. The magnetization was measured in the temperature range 1.9-400 K, in a magnetic field of 50 Oe in zero-field cooled (ZFC) and field cooled (FC) modes with a SQUID magnetometer, and in a magnetic field of 4.83 kOe at increasing temperatures up to 1100 K. The field dependence of the magnetization at 4.2 K was measured up to 140 kOe using a string magnetometer, and up to 370 kOe in a pulsed magnetic field, with a pulse duration of 10 ms [14]. The hysteresis loops were recorded with a SQUID magnetometer at 1.9 K, applying fields up to 50 kOe.

Results and discussion

The results of the crystallographic investigations are presented in Table 1. In most cases, the crystal structure is the same for the off-stoichiometric as for the stoichiometric compounds and the change of composition does not modify substantially the lattice parameters. Exceptions are the Ce and Tb alloys. For $Ce_{2.1}Co_{16.9}Si$ studied here, the hexagonal Th_2Ni_{17} type was observed, whereas the rhombohedral Th_2Zn_{17} type was reported for $Ce_2Co_{16}Si$ in [2]. The reason for this could be different valence state of Ce. In the Tb compound the substitution of Si for Co produces a partial disorder in the structure (towards the hexagonal $TbCu_7$ type), and Si atoms enter the crystallographic positions that form dumbbells [9]. The lattice parameters do not change monotonically as the lanthanide element is changed and the lanthanide contraction is not seen.

The results of the magnetic measurements are presented in Figs. 1-4. The temperature dependence of the magnetization of the alloys at T = 300-1100 K, obtained in a magnetic field of 4.83 kOe, is shown in Fig. 1. The Curie points obtained in the present experiment from dM/dT vs. T plots and literature data are listed in Table 2. One can see that the deviation from the stoichiometry results in a decrease of the Curie points. The highest Curie temperature was measured for the La alloy, and the decrease observed on replacing lanthanum by heavier members of the lanthanide family indicates a strong competition between the magnetic moments of the cobalt and lanthanide sublattices. The small difference between the Curie points of the La and Pr alloys seems to indicate that the latter element is very weakly magnetic. The considerable deviation of T_C of the Ce compound with respect to that of $Ce_2Co_{16}Si$ [2] is another indication of the possible existence of different valence states of Ce in these materials. The $M(T)$ plots for the majority of the compounds exhibit a monotonous decrease up to T_C, except for the Gd

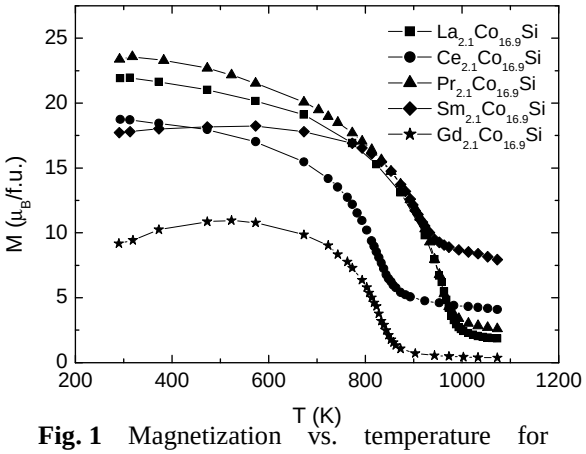
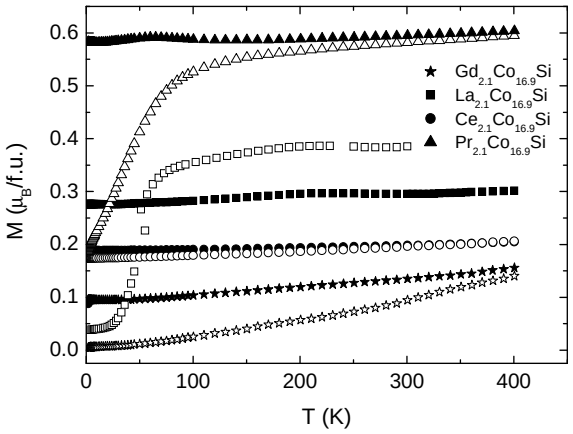
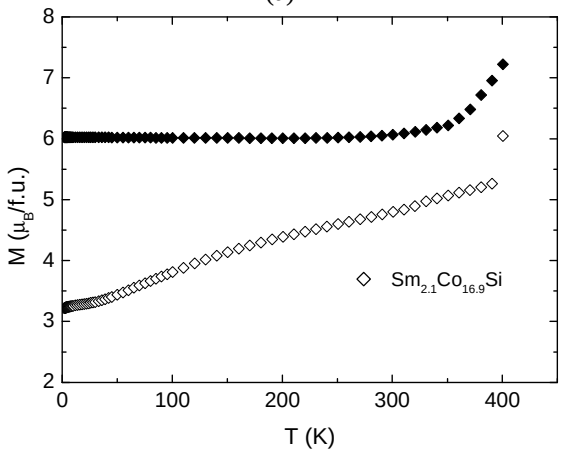


Fig. 1 Magnetization vs. temperature for $Ln_{2.1}Co_{16.9}Si$ alloys at T = 300-1100 K measured in a magnetic field of 4.83 kOe.

compound. The reason for this may be a domain effect. Fig. 2 shows the temperature dependence of magnetization at temperatures 1.9-400 K for La, Ce, Pr and Gd (a), and Sm (b) alloys. The measurements were performed in ZFC mode (open symbols) in 50 Oe and in FC mode, cooled and heated in 50 kOe (full symbols). All compounds, except with Ce, exhibit a very pronounced thermal hysteresis, with sharp critical temperatures for the La, Pr, and Sm alloys. This type of behavior prevents us from concluding firmly that domain phenomena play a significant role. Fig. 3 shows the field dependence of the magnetization (hysteresis loops) at T = 1.9 K. All compounds exhibit negligible hysteresis and remanence and are saturated in relatively low fields. Note that an extremely flat $M(B)$ dependence is observed for the Gd alloy. This behavior may be accompanied by a relatively low magnetocrystalline anisotropy for the Gd compound, and an investigation of the anisotropy of these materials is planned for the near future. The saturation magnetic moments are listed in Table 2. The values obtained in all the experiments are roughly similar, although the



(a)



(b)

Fig. 2 Magnetization vs. temperature for the (a) $Ln_{2.1}Co_{16.9}Si$ alloys (Ln = La, Ce, Pr, Gd) and (b) $Sm_{2.1}Co_{16.9}Si$ alloy at T = 1.9-400 K measured in ZFC (open symbols) and FC (full symbols) modes in a magnetic field of 50 Oe.

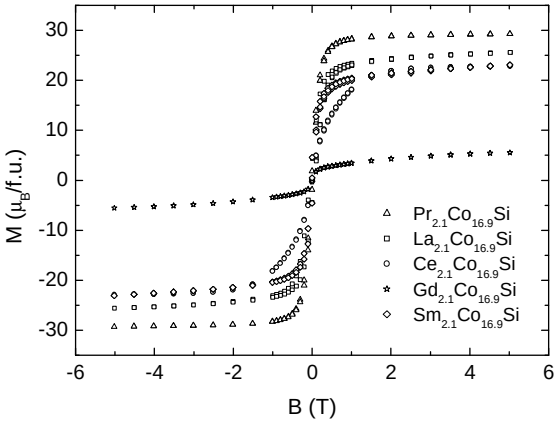


Fig. 3 Magnetization vs. magnetic field for $Ln_{2.1}Co_{16.9}Si$ alloys at T = 1.9 K (hysteresis loops).

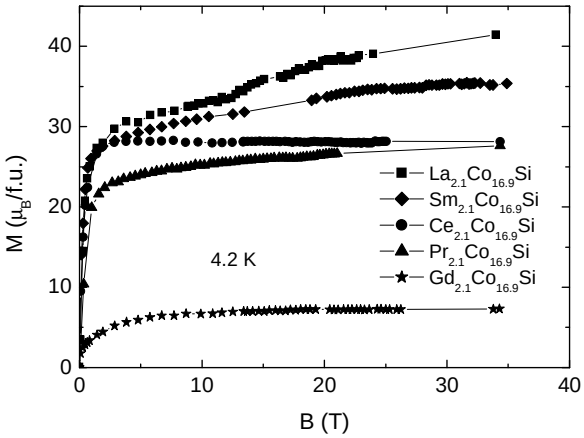


Fig. 4 Magnetization vs. magnetic field for $Ln_{2.1}Co_{16.9}Si$ alloys at T = 4.2 K in pulsed magnetic field with a pulse duration of 10 ms.

saturation magnetic moments for the off-stoichometric alloys are slightly higher, except for the Gd compound. The general tendency observed in all the experiments in moderate fields is the same and the highest saturation moment was determined for the Pr compound. However, the examination of Fig. 4, in which the magnetization (magnetic moment) vs pulsed magnetic field is presented, leads to a different conclusion. As it is seen from Table 2, the highest saturation moment is observed for the La alloy and the magnetization is still increasing as the magnetic field increases. To a lesser extent, similar behavior is observed for the Sm compound, and the saturation moment is not much lower than for the former material. The reason for these properties can still not be completely understood. The magnetization of the Ce and Pr alloys reaches saturation reasonably fast and the saturation moments of these materials are fairly close. Similarly, in the low-field measurements the saturation magnetic moment is the lowest for the Gd compounds, which suggests the possibility of compensation of the magnetic moments between various sublattices.

Table 2 Curie points for the $Ln_2Co_{16}Si$ and $Ln_{2.1}Co_{16.9}Si$ alloys.

Ln	La	Ce		Pr		Sm	Gd	
Alloy	$La_{2.1}Co_{16.9}Si$	$Ce_2Co_{16}Si$	$Ce_{2.1}Co_{16.9}Si$	$Pr_2Co_{16}Si$	$Pr_{2.1}Co_{16.9}Si$	$Sm_{2.1}Co_{16.9}Si$	$Gd_2Co_{16}Si$	$Gd_{2.1}Co_{16.9}Si$
T_C [K]	963	903	838	1001	953	898	1080	828
m_{sat} [μ_B/f.u.], low field (5 T)	25.0	20.88	22.0	27.1	29.7	22.0	10.0	6.0
m_{sat} [μ_B/f.u.], high pulsed field (34 T)	39.5		28.2		27.3	35.5	7.5	
Ref.	this work	[2]	this work	[3]	this work	this work	[5]	this work

Conclusions

The present research confirms earlier observations that substitution of Si for Co does not improve the magnetic properties of Ln_2Co_{17} alloys. The deviation from the stoichiometry $Ln_2Co_{16}Si$ decreases markedly the Curie points, but increases the saturation magnetization (magnetic moment) only moderately. Without more detailed structural investigations it is not possible to draw definite conclusions concerning the reasons for such a behavior.

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