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The crystal structure and magnetic behaviour of the ternary rare earth compounds $RE_2Nb_3X_4$ with RE ≡ rare earth and X ≡ Si, Ge

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Abstract

New compounds $RE_2Nb_3X_4$ have been prepared and characterised for X ≡ Si(RE ≡ Tb, Dy, Ho, Er, Tm, Lu and Y) and X ≡ Ge (RE ≡ Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y). From room temperature X-ray powder diffraction analyses, the silicide alloys were found to crystallise as the $Sc_2Re_3Si_4$ type (ordered Zr_5Si_4 type; space group $P4_12_12$), whilst the germanide compounds crystallised with the $Ce_2Sc_3Si_4$, i.e. the ordered Sm_5Ge_4, type of structure (space group *Pnma*). Magnetic susceptibilities were measured in the temperature range from 5 to 550 K. (Gd, Tb, Dy, Ho, Yb)$_2$Nb$_3$Ge$_4$ and (Tb, Dy)$_2$Nb$_3$Si$_4$ are found to order antiferromagnetically below $T = 20$ K. The Lu and Y containing compounds are temperature-independent Pauli paramagnets.

Keywords: Germanides; Silicides; Rare earths; Magnetism

1. Introduction

In the course of a systematic search for new ternary uranium or rare earth silicides or germanides with atomic ratio 2:3:4, we recently reported on four series of compounds with two different structural types: $U_2Mo_3Si_4$ [1,2] and $Ce_2Sc_3Si_4$ (ordered Sm_5Ge_4) [3,4]. The $Sc_2Re_3Si_4$ type was found in the $U_2Nb_3Si_4$ compound [5], and will be the subject of a forthcoming paper [6]. The investigation of the existence of new compounds in the series $RE_2Nb_3Si_4$ and $RE_2Nb_3Ge_4$, their crystallographic characterisation and magnetic studies are the subject of the present work.

2. Experimental details

All the alloys, each with a total mass of 0.5–1 g, were prepared by arc melting ingots and compacted powders of the constituent elements from the nominal composition $RE_{22.2}Nb_{33.3}X_{44.4}$, but attempts with RE ≡ Yb were made at 900 °C in a vacuum sealed quartz tube. Materials used were commercially available as high purity elements: rare earth metals in the form of ingots (Auer-Remy, purity 99.9%), niobium as a compacted powder (Johnson-Matthey, purity 99.99%) and silicon as lumps (Alfa-Ventron, purity 99.999%). To ensure homogeneity, the alloy pellets were flipped over and remelted several times using electric currents as low as possible to minimise weight losses (below 1 mass%) by evaporation.

Lattice parameters and standard deviations were obtained from a least-squares refinement of room temperature X-ray Guinier–Huber powder data.

The magnetic measurements were performed in the temperature range $5\,K < T < 100\,K$ by use of an a.c. susceptometer (Lake-Shore, a.c. field 1 mT, 133.3 Hz) as well as a pendulum Faraday magnetometer SUS10 above liquid nitrogen temperature up to 550 K and in external fields varying from 0.75 to 1.3 T.

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3. Results and discussion

3.1. Phase formation and crystallochemical characterisation

Considering the existence of the two series $RE_2Mo_3Si_4$ [2,7] and $RE_2Mo_3Ge_4$, [3], RE ≡ Gd→Lu, we started our investigation with the synthesis of the Nb-homologues with the rare earth elements from Sm to Lu. As shown in Tables 1 and 2, our attempts were successful for a large number of rare earths (seven and nine respectively).

X-ray powder diffraction analyses showed, with respect to the position and intensity of the reflections in the Guinier photographs, that silicides crystallise like $U_2Nb_3Si_4$, i.e. with the $Sc_2Re_3Si_4$ type (ordered Zr_5Si_4), whilst germanides crystallise like $U_2Nb_3Ge_4$, i.e. with $Ce_2Sc_3Si_4$ type (ordered Sm_5Ge_4). This behaviour is not similar to the one encountered with the $RE_2Mo_3X_4$ series, where the silicides were isotypic to the $U_2Mo_3Si_4$ whilst the germanides did not crystallise with $U_2Mo_3Ge_4$ structure. No superstructure reflections have been encountered from X-ray powder data. Some traces of secondary phases, however, were indexable, particularly Nb_5Si_3 and RE_2O_3.

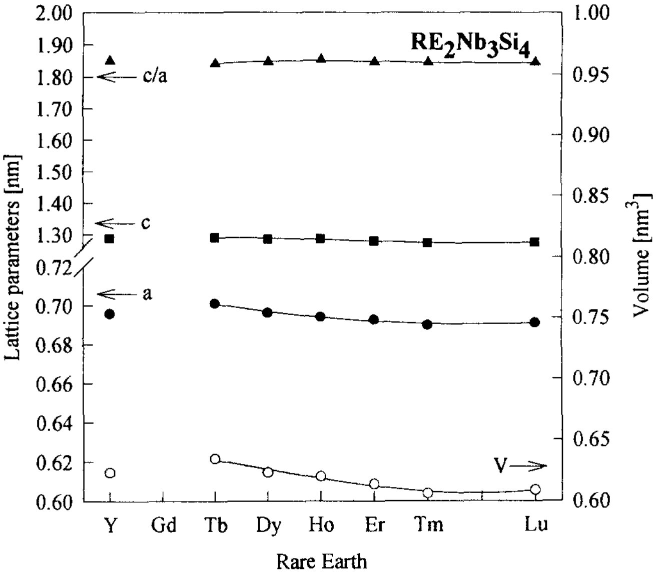

Fig. 1. Lattice parameters vs. rare earths for $RE_2Nb_3Si_4$.

Figs. 1 and 2 show plots of the unit-cell dimensions of the phases $RE_2Nb_3Si_4$ and $RE_2Nb_3Ge_4$ vs. the rare earths. They reflect the expected lanthanoid contraction. Only slight deviations from this trend are encountered, probably due to the varying degrees of non-stoichiometry, consistent with the appearance of

Table 1
Crystallographic and magnetic data of the ternary $RE_2Nb_3Si_4$ compounds (structure type $Sc_2Re_3Si_4$ (ordered Zr_5Si_4); space group $P4_12_12$, D_4^4, No. 92; origin at 2_11 (1,2))

Compound	Lattice parameters (nm)		c/a	V (nm^3)	μ_{eff} (μ_B)	μ_{theo} (μ_B)	θ_p (K)	T_N (K)
	a	c						
$Y_2Nb_3Si_4$	0.6959(5)	1.287(2)	1.8498	0.623(1)	TIP			
$Tb_2Nb_3Si_4$	0.7011(6)	1.291(2)	1.8415	0.634(1)	9.0	9.7	−6	19.0
$Dy_2Nb_3Si_4$	0.6963(9)	1.286(2)	1.8465	0.623(2)	10.2	10.6	−0.4	5.0
$Ho_2Nb_3Si_4$	0.6942(6)	1.287(2)	1.8538	0.620(1)	10.3	10.6	−0.4	
$Er_2Nb_3Si_4$	0.6928(2)	1.2792(7)	1.8465	0.6140(5)	9.4	9.6	−5	
$Tm_2Nb_3Si_4$	0.6900(2)	1.2734(7)	1.8455	0.6063(5)	6.5	7.6	−23	
$Lu_2Nb_3Si_4$	0.6911(6)	1.275(2)	1.8455	0.609(1)	TIP			

Table 2
Crystallographic and magnetic data of the ternary $RE_2Nb_3Ge_4$ compounds (structure type $Ce_2Sc_3Si_4$ (ordered Sm_5Ge_4); space group Pnma, D_{2h}^{16}, No. 62; origin at $\bar{1}$)

Compound	Lattice parameters (nm)			V (nm^3)	μ_{eff} (μ_B)	μ_{theo} (μ_B)	θ_p (K)	T_N (K)
	a	b	c					
$Y_2Nb_3Ge_4$	0.6964(8)	1.3572(13)	0.7182(4)	0.6788(8)	TIP			
$Gd_2Nb_3Ge_4$	0.6998(2)	1.3552(5)	0.7184(3)	0.6813(4)	8.0	7.9	−16	8.5
$Tb_2Nb_3Ge_4$	0.6981(4)	1.3515(6)	0.7156(6)	0.6752(5)	9.8	9.7	−12	7.1
$Dy_2Nb_3Ge_4$	0.6975(4)	1.3510(11)	0.7154(4)	0.6741(6)	10.8	10.6	3	6.2
$Ho_2Nb_3Ge_4$	0.6956(3)	1.3479(4)	0.7131(4)	0.6686(4)	10.8	10.6	4	25.0
$Er_2Nb_3Ge_4$	0.6927(4)	1.3465(7)	0.7116(5)	0.6637(5)	10.4	9.6	−2	
$Tm_2Nb_3Ge_4$	0.6917(4)	1.3416(4)	0.7092(4)	0.6581(4)	7.4	7.6	−7	
$Yb_2Nb_3Ge_4$	0.6937(1)	1.3449(4)	0.7109(2)	0.6632(3)	4.2	4.5	−18	9.2
$Lu_2Nb_3Ge_4$	0.6895(3)	1.3392(5)	0.7071(4)	0.6529(5)	TIP			

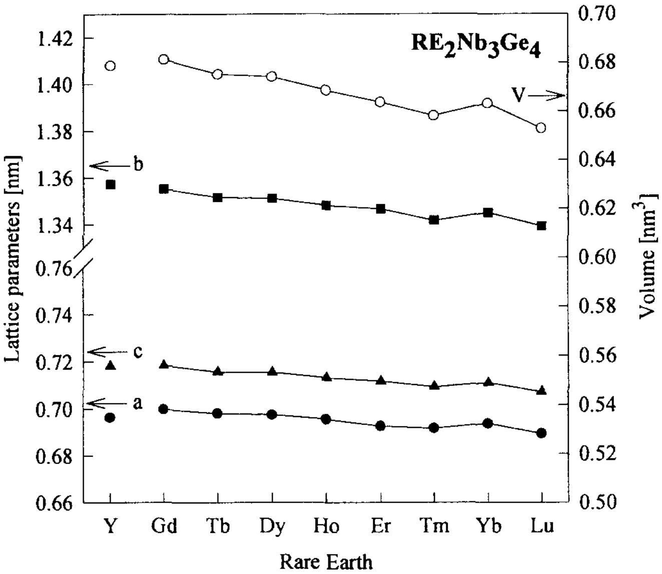

Fig. 2. Lattice parameters vs. rare earths for $RE_2Nb_3Ge_4$.

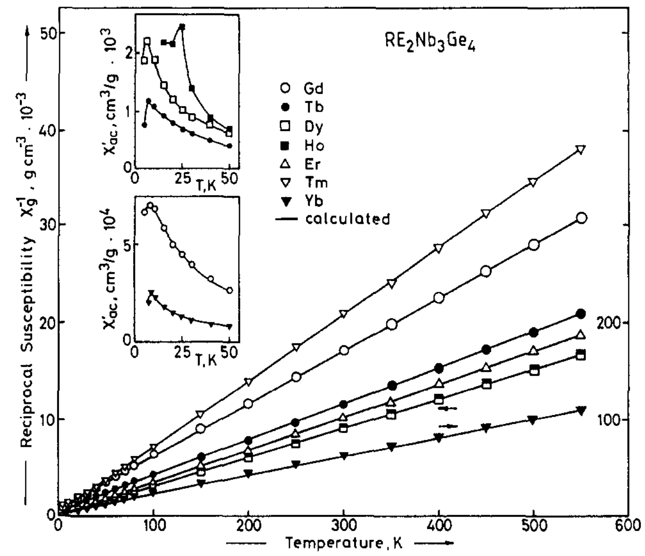

Fig. 4. Reciprocal susceptibility vs. temperature for $RE_2Nb_3Ge_4$. Inset: a.c. susceptibility vs. temperature for $RE_2Nb_3Ge_4$.

small amounts of secondary phases. The small deviation for $Yb_2Nb_3Ge_4$ suggests the presence of divalent ytterbium atoms.

3.2. Magnetism

The magnetic properties of the $RE_2Nb_3X_4$ series of compounds are summarised in Tables 1 and 2 and Figs. 3 and 4.

Fig. 3 shows the temperature dependence of the reciprocal susceptibility for (Tb, Dy, Ho, Er, $Tm)_2Nb_3Si_4$. All compounds reveal an almost linear Curie–Weiss like behaviour for temperatures above around 20 K. The data were fitted by least-squares according to a modified Curie–Weiss law. The calculated paramagnetic effective moments thereby perfectly agree with the theoretical tripositive RE^{3+} ion moments, with the exception of the Tm containing alloy. The slightly reduced $\mu_{eff} = 6.5\ \mu_B$ is possibly caused by the admixture of small amounts of nonmagnetic impurities (secondary phases Nb_5Si_3, etc. as mentioned above), rather than an intermediate valance state of the Tm atom. Furthermore, the (Tb, $Dy)_2Nb_3Si_4$ samples undergo an antiferromagnetic transition at $T = 19$ and 5 K respectively, as shown in the inset of Fig. 3. $Y_2Nb_3Si_4$ and $Lu_2Nb_3Si_4$ are temperature-independent Pauli paramagnets due to the conduction electrons.

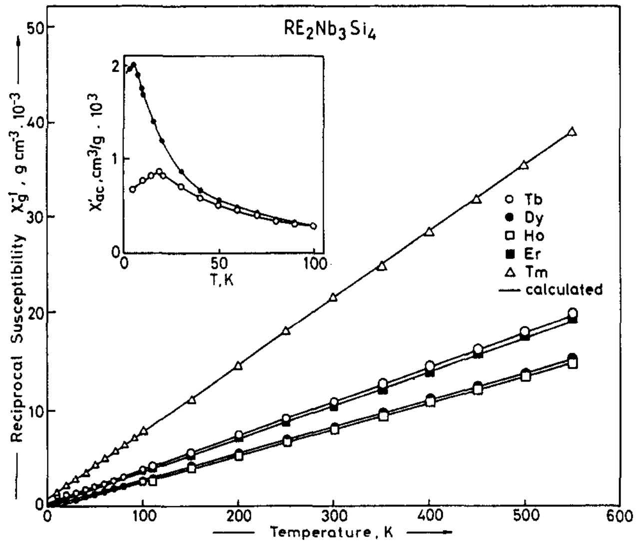

Fig. 3. Reciprocal susceptibility vs. temperature for $RE_2Nb_3Si_4$. Inset: a.c. susceptibility vs. temperature for $Tm_2Nb_3Si_4$ and $Dy_2Nb_3Si_4$.

The germanides (Gd, Tb, Dy, Ho, Er, Tm, $Yb)_2Nb_3Ge_4$ reveal similar magnetic properties to the silicides above. Fig. 4 again proves a Curie–Weiss like temperature dependence of the inverse susceptibilities for temperatures above around 30 K. The calculated μ_{eff} thereby match with the theoretical free ion moments, which is also true for the Tm containing compound (see Table 2). In case of $Yb_2Nb_3Ge_4$ the slightly reduced μ_{eff}, as well as the negative θ_p value, seems to stem from an intermediate valence state of the ytterbium atom ($Yb^{3+} \leftrightarrow Yb^{2+}$ adopting the $^2F_{7/2}$ and $^1S_0$ ground state configurations respectively), which is also supported by the observed volume increase (see Fig. 2). For the Gd, Tb and Dy, as well as the Ho and Yb containing samples, antiferromagnetic ordering is observed in the low temperature regime, as shown in the insets of Fig. 4. As the Néel points roughly scale with the de Gennes factor $(g - 1)^2 J(J +$

1), the RKKY indirect exchange coupling mechanism via the conduction electrons seems to be the driving force of the antiparallel spin alignment of the rare earth sublattice. $Y_2Nb_3Ge_4$ and $Lu_2Nb_3Ge_4$ are found to be temperature-independent Pauli paramagnets due to the non-magnetic ground state of the yttrium and lutetium atoms.

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