# On the crystal structure and magnetic properties of the ternary rare earth compounds $RETSb_2$ with $RE \equiv rare$ earth and $T \equiv Ni$ , Pd, Cu and Au

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#### Abstract

Novel compounds RETSb<sub>2</sub> have been prepared and characterized for  $T \equiv Cu$  (RE $\equiv$ rare earth from La to Lu), Ni (RE $\equiv$ La to Ho), Pd (RE $\equiv$ La to Tb) and Au (RE $\equiv$ La to Sm). From X-ray powder diffraction analyses all compounds were found to crystallize as the ZrCuSi<sub>2</sub> type. Magnetic susceptibilities were generally measured in the temperature range from 4 to 100 K. YCuSb<sub>2</sub> and LaTSb<sub>2</sub> are temperature-independent paramagnets. RETSb<sub>2</sub> compounds are found to order antiferromagnetically below T=20 K. PrPdSb<sub>2</sub> and TbPdSb<sub>2</sub> undergo metamagnetic transitions, whereas PrCuSb<sub>2</sub> and ErCuSb<sub>2</sub> are simple ferromagnets. The Sm-containing compounds are typical Van Vleck paramagnets owing to the closely spaced multiplets.

#### 1. Introduction

Our concern for heavily correlated electron systems in relation to weak magnetic rare earth-metal interactions has prompted us to investigate systematically the formation and structural chemistry of ternary compounds with the formula RETSb<sub>2</sub>, where T is a metal of the Ni and Cu group. The main interest naturally focused on the interrelation between structural stability, crystal chemistry and magnetic properties. The current study is based on knowledge of the formation of several compounds RENiSb<sub>2</sub> for the light rare earth metals, Ce, Pr, Nd and Sm [1]. Pankevich *et al.* [1] have provided crystallographic characterization; however, no magnetochemical studies have been carried out so far.

#### 2. Experimental details

The alloys, each with a total mass of 0.5–1 g, were synthesized by argon arc melting ingots of the elements starting from the nominal composition  $RE_{25}T_{25}Sb_{50}$ .

The materials used were commercially available as high purity elements: rare earth metals were in the form of ingots (99.9% pure; Auer–Remy GmbH, Germany); nickel and copper were in form of wire 2 mm thick (99.9% Ni; Goodfellow, UK) or 8 mm rod respectively (99.9% Cu; Johnson–Matthey&Co., UK); Sb was obtained as 10 mm rod (99.9% pure) from Johnson–Matthey & Co. For further details of the sample preparation, the X-ray powder techniques employed for structural characterization as well as the equipment and type of magnetic measurements performed, the reader is referred to our recent publications on the related series of compounds REFeSb<sub>2</sub>, and RECoSb<sub>2</sub> [2] and/or similar subjects [3].

Some technical details on the duration and temperature of the homogenizing anneal of the alloys prior to quenching of the silica capsules in water are given in Table 1. The magnetic susceptibilities were generally measured in the temperature range 4–100 K; the isothermal magnetization at T=5 K was determined in external fields of up to 3 T with a superconducting quantum interference device.

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TABLE 1. Crystallographic and magnetic data of ternary compounds RETSb<sub>2</sub>,  $T \equiv Ni$ , Pd, Cu on Au (Structure type, ZrCuSi<sub>2</sub>; space group, P4/nmm, D<sup>7</sup><sub>4h</sub>, No. 129; origin at centre; Z=2)

Compound	Heat treatment (°C)	Lattice parameters (nm)		c/a	V	T <sub>N</sub>	Θ <sub>p</sub>	μ <sub>eff</sub>	Reference
		a	с		(nm <sup>2</sup> )	(K)	(K)	(μ <sub>B</sub> )	
LaNiSb <sub>2</sub>	600	0.44269(10)	0.9876(6)	2.2309	0.1935(1)	TIP			This work
CeNiSb <sub>2</sub>	600	0.43934(12)	0.9750(3)	2.2192	0.1882(1)	<4.0	0.0	1.44	This work
	600	0.4409(2)	0.9749(4)	2.2112	0.1895				1
PrNiSb <sub>2</sub>	600	0.43853(9)	0.9699(6)	2.2116	0.1865(1)	6.0	-4.0	4.00	This work
	600	0.4379(4)	0.9672(5)	2.2087	0.1855				1
NdNiSb <sub>2</sub>	600	0.43674(10)	0.9629(4)	2.2048	0.1837(1)	<4.0	- 12.0	4.30	This work
	600	0.4364(3)	0.9614(4)	2.2030	0.1831				1
$SmNiSb_2$	600	0,43406(10)	0.9523(6)	2.1940	0.1794(1)			1.80ª	This work
	600	0.4335(2)	0.9513(3)	2.1945	0.1788				1
GdNiSb <sub>2</sub>	800	0.43345(11)	0.9452(4)	2.1806	0.1775(1)	9.0	- 44.0	9.60	This work
TbNiSb <sub>2</sub>	800	0.43201(17)	0.9361(4)	2.1669	0.1747(2)	12.0	- 44.0	10.80	This work
DyNiSb <sub>2</sub>	600	0.43092(9)	0.9305(6)	2.1593	0.1728(1)	10.0	- 27.0	13.00	This work
HoNiSb <sub>2</sub>	800	0.42989(8)	0.9257(5)	2.1533	0.1710(1)	<4.0	- 12.0	10.20	This work
LaPdSb <sub>2</sub>	600	0.45309(14)	0.9989(7)	2.2045	0.2051(2)	TIP			This work
CePdSb <sub>2</sub>	600	0.44899(10)	0.9893(6)	2.2034	0.1989(2)	<4.0	- 65.0	3.04	This work
PrPdSb <sub>2</sub>	600	0.44707(10)	0.9790(5)	2.1898	0.1957(1)	8.0 <sup>b</sup>	-13.0	4.00	This work
NdPdSb <sub>2</sub>	600	0.44647(6)	0.9738(4)	2.1802	0.1940(1)	<4.0	-3.0	3.50	This work
SmPdSb <sub>2</sub>	600	0.44315(12)	0.9627(7)	2.1723	0.1891(1)			1.50 <sup>a</sup>	This work
GdPdSb <sub>2</sub>	600	0.44150(9)	0.9567(7)	2.1686	0.1871(1)	15.0	-41.0	7.90	This work
TbPdSb <sub>2</sub>	600	0.44097(10)	0.9480(6)	2.1498	0.1843(1)	18.0 <sup>b</sup>	- 30.0	9.80	This work
YCuSb <sub>2</sub>	800	0.42617(8)	0.9903(5)	2.3238	0.1799(1)	TIP			This work
LaCuSb <sub>2</sub>	600	0.43690(9)	1.0376(4)	2.3750	0.1981(1)	TIP			This work
CeCuSb <sub>2</sub>	600	0.43378(6)	1.0233(5)	2.3590	0.1925(1)	8.0	-7.0	2.50	This work
PrCuSb <sub>2</sub>	600	0.43250(5)	1.0159(5)	2.3490	0.1900(1)	5.0°	3.5	3.60	This work
NdCuSb <sub>2</sub>	600	0.43118(7)	1.0111(5)	2.3450	0.1880(1)	< 4.0	- 9.0	3.70	This work
SmCuSb <sub>2</sub>	600	0.42939(6)	0.9999(3)	2.3286	0.1844(1)			1.30ª	This work
GdCuSb <sub>2</sub>	600	0.42783(5)	0.9946(3)	2.3247	0.1821(1)	12.0	-33.0	8.90	This work
TbCuSb <sub>2</sub>	800	0.42683(9)	0.9877(7)	2.3140	0.1799(1)	9.0	-23.0	9.40	This work
DyCuSb <sub>2</sub>	600	0.42669(14)	0.9817(5)	2.3070	0.1787(2)	6.0	9.0	10.30	This work
HoCuSb <sub>2</sub>	600	0.42529(7)	0.9811(5)	2.3058	0.1776(1)	<4.0	-4.0	10.40	This work
ErCuSb <sub>2</sub>	800	0.42433(13)	0.9788(3)	2.3066	0.1762(1)	< 4.0 <sup>d</sup>	-3.0	9.80	This work
TmCuSb <sub>2</sub>	600	0.42437(8)	0.9742(6)	2.2956	0.1754(1)	<4.0	-3.0	7.30	This work
YbCuSb <sub>2</sub>	600	0.43229(14)	0.9689(6)	2.2413	0.1811(2)				This work
LuCuSb <sub>2</sub>	Arc	0.42347(5)	0.9705(5)	2.2917	0.1740(1)				This work
LaAuSb <sub>2</sub>	800	0.44363(10)	1.0434(4)	2.3522	0.2052(3)	TIP			This work
CeAuSb <sub>2</sub>	400	0.44081(3)	1.0339(2)	2.3455	0.2009(1)	6.0	2.0	2.30	This work
PrAuSb <sub>2</sub>	800	0.43933(9)	1.0290(3)	2.3423	0.1987(1)	9.0	- 6.0	3.90	This work
NdAuSb <sub>2</sub>	800	0.43870(9)	1.0192(3)	2.3233	0.1962(1)	<4.0	- 9.6	3.40	This work
$SmAuSb_2$	600	0.43653(8)	1.0134(5)	2.3215	0.1931(1)	_		1.50 <sup>c</sup>	This work

TIP temperature-independent paramagnet.

\*Effective moment at 80 K.

<sup>b</sup>Metamagnetism,  $\mu_0 H_{crit} > 2.5$  T.

<sup>c</sup>Ferromagnetic, magnetic moment ( $\mu_0 H=3$  T at 5 K)=1.7  $\mu_B$ . <sup>d</sup>Ferromagnetic, magnetic moment ( $\mu_0 H=3$  T at 5 K)=5.6  $\mu_B$ .

#### 3. Results and discussion

## 3.1. Formation of compounds and crystallochemical characterization

With respect to the knowledge of the existence of several Ni-containing compounds  $RENiSb_2$ ,  $RE \equiv Ce$ , Pr; Nd or Sm [1], we commenced our investigation with the synthesis of these compounds in a pure phase form. X-ray powder diffraction analyses in all cases

confirmed the structure type of  $ZrCuSi_2$ , as suggested by Pankevich *et al.* [1]. Our lattice parameter data agree well with those reported earlier (see Table 1 for comparison). The second step was to check the existence of further Ni-containing compounds with the entire range of the rare earth metals from Sc to Lu. Our attempts were successful for only a limited number of rare earth elements namely La, Gd, Tb, Dy and Ho, which were able to form isostructural compounds (see Table 1). With respect to the obviously wide range of RETSb<sub>2</sub> compounds (note for example the existence of REFeSb<sub>2</sub> and RECoSb<sub>2</sub> [2]), we finally probed all combinations of homologous compounds with the Ni group (Pd and Pt) and the neighbouring Cu group (Cu, Ag and Au). These attempts to synthesize a  $RETSb_2$ compound were successful when T was an element such as Pd, Cu or Au, but with varying stability limits for each of these series (see Table 1). The results of our X-ray powder analyses with respect to the position and the intensity of the reflections in the Guinier photographs (Cu K $\alpha_1$ ) unambigously confirmed isotypism with the crystal structure of ZrCuSi<sub>2</sub>. No superstructure reflections have been encountered from X-ray powder data. The X-ray powder intensities observed were generally found to be in fine agreement with the corresponding calculated values, employing the atom parameter set derived from a single-crystal study of NdFeSb<sub>2</sub> [2] (RE in 2c  $(\frac{1}{4}, \frac{1}{4}, 0.2580)$  T in 2b  $(\frac{3}{4}, \frac{1}{4}, \frac{1}{2})$ , Sb(1) in 2a  $(\frac{3}{4}, \frac{1}{4}, 0)$  and Sb(2) in 2c  $(\frac{1}{4}, \frac{1}{4}, 0.6265)$ . This is particularly true for all Ni, Cu- and Pd-containing compounds. Significant discrepancies between observed and calculated X-ray powder intensities are, however, obvious for all the compounds of the series REAuSb<sub>2</sub>, indicating significant changes in the atom parameter set with respect to the Cu, Ni and Pd homologues. A proper atom parameter set was obtained from a Rietveld refinement of X-ray intensities recorded from a flat sample specimen of SmAuSb<sub>2</sub> in a D5000 Siemens automatic powder diffractometer (range from 10° to 120 ° in 2 $\theta$ ;  $\Delta\theta = 0.01^{\circ}$ ). With these parameters (Sm in 2c  $(\frac{1}{4}, \frac{1}{4}, 0.2462)$  and Sb(2) in 2c  $(\frac{1}{4}, \frac{1}{4}, 0.6840)$  the calculated X-ray powder intensities for all Au-containing phases are corresponding well to the experimental observation. Some traces of secondary phases, however, were indexable particularly  $RE_3Cu_3Sb_4(Y_3Au_3Sb_4type)$ , NiSb (NiAs type) in the alloys with  $RE \equiv Tb$ , Dy or Ho,  $PdSb_2$  (FeS<sub>2</sub> type) for RE=Gd or Tb and RECuSb for RE=Ho or Tm. No ZrCuSi<sub>2</sub>-type compounds have been observed for RERuSb<sub>2</sub>, RERhSb<sub>2</sub>, REOsSb<sub>2</sub>, REIrSb<sub>2</sub> and REPtSb<sub>2</sub>, whereas forthcoming papers [4, 5] will report on the structural chemistry and magnetism of three further series of compounds REMnSb<sub>2</sub>,  $REZnSb_2$  and  $REAgSb_2$  which we also observed to crystallize with the ZrCuSi<sub>2</sub> type of structure.

#### 3.2. Structural chemistry

The plot of the unit-cell dimensions of the various isostructural phases  $\text{RETSb}_2 vs.$  the rare earths reflects the expected lanthanoid contraction for each T metal series of compounds (Fig. 1). Only slight deviations from this trend are encountered for the cerium compounds in the case of the three phases CeNiSb<sub>2</sub>, CePdSb<sub>2</sub> and CeAuSb<sub>2</sub>, whereas no significant deviation was obvious for CeCuSb<sub>2</sub>, indicating some intermediate

valence behavior for the aforementioned group of compounds, but a tripositive magnetic ground state for CeCuSb<sub>2</sub>. Deviations, however, are pronounced for YbCuSb<sub>2</sub>, thereby suggesting a substantial presence of divalent ytterbium atoms. The observed scatter of the lattice parameter values for some of the rare earth compounds is probably due to the varying degree x of non-stoichiometric  $\text{RET}_{1-x}\text{Sb}_2$  at the T-rich end of a homogeneous range consistent with the appearance of small amounts of secondary phases (see section 3.1).

For the 3d elements Ni and Cu the largest number of representatives is encountered within each series of compounds also including YCuSb<sub>2</sub> whilst, in case of  $T \equiv Pd$  or Au, almost only the large and early rare earth members are able to form a ZrCuSi<sub>2</sub>-type compound (see Table 1 and Fig. 1). With respect to the unit-cell volume of the homologous rare earth phases RECuSb<sub>2</sub>, the unit-cell volume of YCuSb<sub>2</sub> compares with that of the Gd or Tb members, thereby being slightly larger than the usually observed size relation with Tb or Dy phases. The unit-cell dimensions for  $YCuSb_2$  with Y as a non-lanthanoid element with empty 4f shell, however, reveal a significant deviation from this correspondence (see Fig. 1). Despite the fact that the Ni series of compounds RENiSb<sub>2</sub> extends from La to Ho, surprisingly no homologous yttrium compound is formed. Instead, the alloy "YNiSb<sub>2</sub>" after an anneal at 600 °C was found to consist of two phases, namely NiSb (a=0.3926(7) nm and c=0.5134(4) nm; NiAs type) and YSb (a = 0.61707(5) nm; NaCl type). Similarly, "ErNiSb<sub>2</sub>" was of a two-phase nature; ErSb (a=0.6146(3) nm; NaCl type; diffuse) and NiSb  $(a = 0.392 \ 82(7) \text{ nm and } c = 0.5134(3) \text{ nm}).$ 

#### 3.3. Magnetism

The magnetic behaviors of the RETSb<sub>2</sub> ternary compounds are summarized in Fig. 2–4 and Table 1. The magnetic data deduced from the experiments bear a high degree of resemblance for the compounds with the various T elements (Ni, Pd, Cu and Au).

(a) The La-containing compounds as well as YCuSb<sub>2</sub> are typical temperature-independent paramagnets with  $\chi_g$  values of the order of  $10^{-6}$  cm<sup>3</sup> g<sup>-1</sup>. No superconductivity was observed down to 4 K.

(b) The Sm-containing compounds show the characteristic Van Vleck type of paramagnetism owing to the low-lying multiplets.

(c) The samples containing Ce, Pr, Nd and Gd to Tm exhibit antiferromagnetic ordering at temperatures below 20 K. Both the Neel temperatures and the paramagnetic Curie temperatures roughly scale with the de Gennes factor  $J(J+1)(g-1)^2$ , indicating indirect exchange interactions (Ruderman-Kittel-Kasuya-Yosida) to be the dominating force in the coupling mechanism. PrPdSb<sub>2</sub> and TbPdSb<sub>2</sub> furthermore reveal



Fig. 1. Lattice parameters and volumes of the compounds RETSb<sub>2</sub>.



Fig. 2. Molar susceptibilities vs. temperature for RENiSb<sub>2</sub>, REPdSb<sub>2</sub> and RECuSb<sub>2</sub>.



Fig. 3. Molar susceptibilities vs. temperature for REAuSb<sub>2</sub>.



Fig. 4. Magnetization vs. magnetic field for  $PrPdSb_2$  and  $PrCuSb_2$ and  $ErCuSb_2$  at T=5 K.

metamagnetism, *i.e.* the spin system is reoriented toward ferromagnetism at rather high external fields ( $\mu_0 H > 2.5$  T). This behavior is particularly indicated by the increase in the magnetization vs. magnetic field (see Fig. 4). PrCuSb<sub>2</sub> and ErCuSb<sub>2</sub> are found to order ferromagnetically; however, they are also very probably metamagnets with rather low critical fields ( $\mu_0 H \le 0.1$  T). The ordered moments were derived from the magnetization curves (Fig. 4) and found to be approximately one half of the theoretical value gJ, which is obvious as the ordering temperatures for both compounds are below  $T_c \le 5$  K and thus full saturation cannot be reached.

It is worthwhile mentioning that the observed paramagnetism is generally due to the tripositive ground state of the rare earth atoms. The discrepancy of some of the observed effective and the theoretical magnetic moments, however, is simply caused by a deflection of linearity of the reciprocal susceptibility curve vs. temperature in the low temperature regime (short-range order effects). Furthermore the slightly reduced moment for CeAuSb<sub>2</sub> possibly stems from Kondo-lattice behavior.

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