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Very weak itinerant ferromagnetism in the new $Lu_3Co_{8-x}Sn_4$ compound ($x = 0.23$)

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Abstract

The crystal structure of the new compound $Lu_3Co_{8-x}Sn_4$ ($x = 0.23$) was determined by using a single-crystal diffraction method. The structure of $Lu_3Co_{8-x}Sn_4$ is a distorted variant of the $BaLi_4$ structure type: space group $P6_3mc$, $a = 8.746(3)$ Å, $c = 7.432(2)$ Å, $Z = 2$. The coordination number of the lutetium atom is 18; for the tin and cobalt atoms the coordination polyhedra are either distorted icosahedra or trigonal prisms. The magnetic properties of $Lu_3Co_{8-x}Sn_4$ are presented and discussed. This compound is a typical very weak itinerant ferromagnet with $T_c = 63$ K and a Co moment of 0.19 μ_B at 4 K, whereas the effective paramagnetic moment reaches 1.86 μ_B/Co.

Keywords: $Lu_3Co_{8-x}Sn_4$; Itinerant ferromagnetism; Magnetic properties; Crystal structure

1. Introduction

When rare earth metals are combined with cobalt and tin, in the cobalt-rich domain, only stannides of the composition RCo_3Sn are formed, with R = Y, Gd–Yb [1]. The crystal structure of these stannides belongs to the $BaLi_4$ type [2] (space group $P6_3/mmc$, with $a = 8.844$ Å, $c = 7.446$ Å for YCo_3Sn). However, these compounds can have a variable cobalt and tin content corresponding to the formula $RCo_{3-x}Sn_{1+x}$ (e.g. $x = 0$–0.25 for the Gd phase). They are magnetically ordered up to 1000 K and the stannides with R = Gd–Tm exhibit compensation points. High Curie temperatures have been justified in terms of the formation of cobalt clusters in the structure.

The lutetium stannide of this composition does not exist, although a lutetium stannide of unknown structure corresponding approximately to the formula $Lu_2Co_5Sn_3$ has been found. Investigations of its crystal structure and magnetic properties are reported in this paper.

2. Experimental

The sample of starting composition $Lu_2Co_5Sn_3$ was prepared by melting of the constituents (Lu, purity 99%; Co 99.99%; Sn, 99.999%) in an arc furnace under argon atmosphere. The sample was annealed at 800°C for 300 h in an evacuated quartz ampoule. A prism-like single crystal was found in the ingot. A preliminary X-ray analysis was made using the Laue and Weissenberg methods. The structure was analysed by means of a DARTCH-1 automatic diffractometer equipped with a back scattering graphite monochromator. The unit cell parameters were refined from the 2θ values of 20 reflections. The crystal structure was solved by direct methods in the space group $P6_3/mc$ using a program from the CSD package [3]. The structure determination and refinement of the position and thermal parameters of atoms based on R value convergence, were calculated up to the final values $R(F) = 0.0382$ and $R(W) = 0.0433$. Measurements of the bulk magnetisation (under magnetic fields up to 8 T) and susceptibility (with applied magnetic field of 0.5 T, in the temperature range 4–300 K) were performed using an extraction magnetometer.

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3. Results and discussion

3.1. Structural properties

The crystallographic data of the compound are listed in Table 1, the position and thermal parameters are listed in Table 2 and the interatomic distances in Table 3. The stoichiometry deduced from the structural refinement, corresponds to the formula $Lu_3Co_8Sn_4$ (instead of $Lu_2Co_5Sn_3$) with $Z = 2$ formula units in the elementary cell. Owing to the existence of vacancies in the Co2 position, the corresponding formula is $Lu_3Co_{7.77}Sn_4$, or $Lu_3Co_{8-x}Sn_4$ ($x = 0.23$). The coordination number (CN) of the Lu atom is 18, for Sn2, Co1, Co3 and Co4 atoms the CN is equal to 12, and the coordination polyhedra are distorted icosahedra. The coordination polyhedra of Sn1 and Co2 atoms are distorted trigonal prisms with four additional atoms. Note that these prisms are strongly distorted.

The considered structure belongs to a new type ($Lu_3Co_{8-x}Sn_4$ type). The projection of the structure on the x–y plane and the coordination polyhedra are represented on Fig. 1. All the Lu–Sn distances are shorter than the sum of the atomic radii of Lu and Sn (3.30 Å), especially for Lu–Sn1 (3.098 Å). A shortening of some Co–Sn and Co–Co distances is also observed.

As mentioned before, the compounds RCo_3Sn (R = Y, Gd–Yb) present a $BaLi_4$ structure type. The lattice parameters of $Lu_3Co_{8-x}Sn_4$ are very close to those of the RCo_3Sn phase, although these structures are different according to the space group: the RCo_3Sn stannides belong to the $P6_3/mmc$ space group, whereas the compound $Lu_3Co_{7.77}Sn_4$ crystallises in the noncentrosymmetric $P6_3mc$ space group. Analysis of the

Table 1
Crystallographic data for $Lu_3Co_{7.77}Sn_4$

Space group	$P6_3mc$
a (Å)	8.746(3)
c (Å)	7.432(2)
Cell volume (Å^3)	492.3(5)
Number of atoms per unit cell	29.5
Calculated density (g cm^{-3})	9.831(9)
Absorption coefficient (cm^{-1})	543.13
Radiation and wavelength (Å)	Mo 0.71069
Diffractometer type	DARTCH^{-1}
Restrictions	$F(hkl) > 4.00$ sig(F)
Weighting scheme	$1/[\mathrm{sig}(F)^2 + 0.0012\,F(\mathrm{obs})^2]$
2θ and $\sin\theta/\lambda$ (max)	69.65 0.804
Number of measured reflections	453
Number of unique reflections	251
R(sig), R(eq)	0.0284, 0.0479
$R(F)$, $R(W)$	0.0382, 0.0412

Table 2
Atomic and thermal parameters for $Lu_3Co_{7.77}Sn_4$

Atom	Site	x	y	z	$B_{is/eq}$	Occupation
Lu	6c	0.5254(1)	$-x$	0	1.05(3)	1
Sn1	2b	1/3	2/3	0.1987(7)	1.06(8)	1
Sn2	6c	0.1720(2)	$-x$	0.7867(4)	1.09(4)	1
Co1	2a	0	0	0.7140(11)	0.76(12)	1
Co2	2b	1/3	2/3	0.850(2)	1.4(2)	0.77
Co3	6c	0.1632(4)	$-x$	0.1579(7)	1.03(7)	1
Co4	6c	0.1026(4)	$-x$	0.4686(6)	0.96(8)	1

Table 3
Interatomic distances (Å) for $Lu_3Co_{7.77}Sn_4$

Lu	2 × Co3	2.997(5)	1 × Co2	3.115(5)2	1 × Sn1	3.263(3)	2 × Lu	3.707(1)
	2 × Co4	3.061(4)	2 × Sn2	3.137(2)	1 × Co2	3.370(12)	2 × Lu	3.795(1)
	1 × Sn1	3.098(4)	2 × Sn2	3.141(3)	2 × Co3	3.489(5)		
Sn1	1 × Co2	2.59(2)	3 × Co3	2.595(5)	3 × Lu	3.097(4)	3 × Lu	3.263(3)
Sn2	1 × Co2	2.489(4)	2 × Co4	2.642(5)	2 × Co3	2.716(5)	2 × Lu	3.137(2)
	1 × Co4	2.587(6)	1 × Co1	2.661(4)	1 × Co3	2.762(7)	2 × Lu	3.141(3)
Co1	3 × Co4	2.397(8)	3 × Co4	2.449(8)	3 × Co3	2.508(4)	3 × Sn2	2.661(4)
Co2	3 × Sn2	2.489(4)	1 × Sn1	2.59(2)	3 × Lu	3.116(5)	3 × Lu	3.368(12)
Co3	1 × Co4	2.485(7)	2 × Co4	2.582(6)	2 × Sn2	2.716(5)	2 × Lu	2.998(4)
	1 × Co1	2.508(4)	1 × Sn1	2.595(4)	1 × Sn2	2.762(7)	2 × Lu	3.489(5)
Co4	1 × Co1	2.397(8)1	1 × Co3	2.485(7)	1 × Sn2	2.587(6)	2 × Co4	2.693(5)
	1 × Co1	2.449(8)	2 × Co3	2.582(7)	2 × Sn2	2.642(5)	2 × Lu	3.061(4)

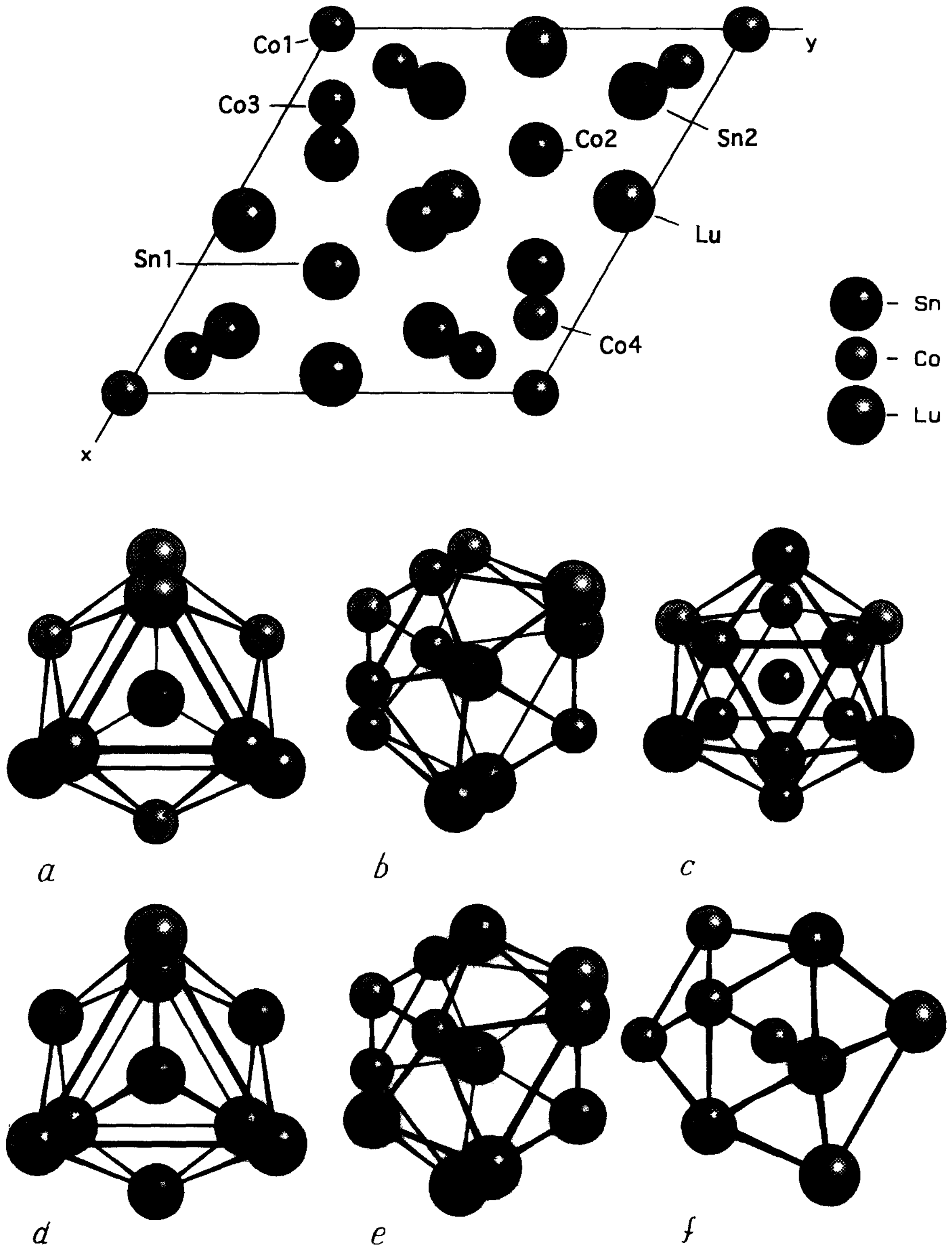

Fig. 1. Projection of the $Lu_4Co_{7.77}Sn_4$ unit cell on the x–y plane and atom coordination polyhedra: (a) Sn1; (b) Sn2; (c) Co1; (d) Co2; (e) Co3; (f) Co4.

two crystal structures shows that they are very close to each other. Hence, one may consider that the crystal structure of $Lu_3Co_8Sn_4$ is derived from the $BaLi_4$ type, according to the ordering of the Co and Sn atoms and to the strong intrinsic distortion. If we compare the atomic sites in both structures, we observe that the Lu atoms occupy the Ba sites; the 4(f) site of the $BaLi_4$ structure (Li2 atoms) is decomposed in two sites 2(b) occupied by Sn1 and Co2, whereas the 12(k) site (Li4 atoms) is decomposed in two 6(c) sites occupied by the Sn2 and Co3 atoms. The Li1 and Li3 sites correspond to the Co1 and Co4 sites respectively.

The $BaLi_4$ structure can be seen as formed by a waved lattice of atoms at different z-values of approximately 0, 0.25, 0.50, and 0.75 of the c parameter [4]. The same lattice representation can be found in the $Lu_3Co_8Sn_4$ structure, becoming more waved in this case. The CN and coordination polyhedra are the same in both structures. Nevertheless, the coordination polyhedra in the $Lu_3Co_8Sn_4$ structure are even more distorted than those of $BaLi_4$ structure.

In the RCo_3Sn stannide, the R atoms occupy the 6(h) Ba atoms sites. The occupation of the Li sites (12(k), 6(h), 4(f), 2(a)) depends on composition. From the powder method analysis of the YCo_3Sn structure, we deduce a statistical distribution of the Co and Sn atoms in the 12(k) sites, the remaining sites being occupied by Co atoms [1]. In $GdCo_{2.8}Sn_{1.2}$ (the compound richest in Sn) it is observed that, except in the 12(k) sites, the Co and Sn atoms are statistically distributed in the 4(f) site (63% Co and 37% Sn, approximately). Finally, the increase in tin content must yield the same amount of Sn and Co atoms in the sites exhibiting a statistical content. However, this induces large modifications in the structure (distortion, deformation) and, as a consequence, a change in the space group occurs. Actually, it is the 4(f) and 12(k) sites of the $P6_3/mmc$ space group that respectively split in two sites, which are occupied by Co and Sn in the $P6_3mc$ space group. From the definitive ordering (site splitting) of the Co and Sn atoms, a special feature may be underlined: the Sn atoms do not contact each other.

The RCo_3Sn series and $Lu_3Co_{7.77}Sn_4$ are the first rare earth compounds with the $BaLi_4$ type structure. Taking into account that the ratio of the R and (Co, Sn) atom radii is much smaller than that of the Ba and Li atom radii, a structure distortion and an enhancement of the c/a ratio in the RCo_3Sn phases is observed ($c/a = 0.807$ in $BaLi_4$ vs. 0.844 in YCo_3Sn). The interatomic distances decrease, and it is probably the 'internal' pressure that provokes the formation of vacancies in the 2(b) Co site. In $Lu_3Co_{7.77}Sn_4$, where the Sn-content is larger (i.e. where the R atom radii of the second components are even closer) a larger increase of c/a is observed (0.850) and, finally, a structure change results.

3.2. Magnetic properties

Isothermal variations of magnetisation as a function of the applied field, measured on a polycrystal, are displayed in Fig. 2 at several temperatures. The magnetisation is always small and strongly field dependent, even in the largest applied field. At 4 K and in an 8 T applied field, the magnetisation reaches 2.21 μ_B/formula unit (f.u.), i.e. 0.28 μ_B/Co. The Arrott plots (M^2 vs. H/M) are shown in Fig. 3. They exhibit a linear variation for each isotherm and their slope is almost temperature independent over a wide temperature range. The Curie temperature ($T_c = 63$ K) corresponds to the isotherm passing through the origin. From the Arrott plots, the spontaneous magnetisation M_s and the reciprocal paramagnetic susceptibility can be deduced at each temperature. Their thermal variations are reported in Fig. 4. At 4 K the spontaneous magnetisation reaches 1.53 μ_B/f.u., i.e. 0.19 μ_B per Co atom. The variation of M_s^2 as a function of T^2, displayed in Fig. 5, is linear.

All these properties of $Lu_3Co_{7.77}Sn_4$ are quite well described in the model of the very weak itinerant ferromagnetism (VWIF) [5,6]. In this model, the exchange interactions are treated within the molecular field approximation, and thermal effects are consid-

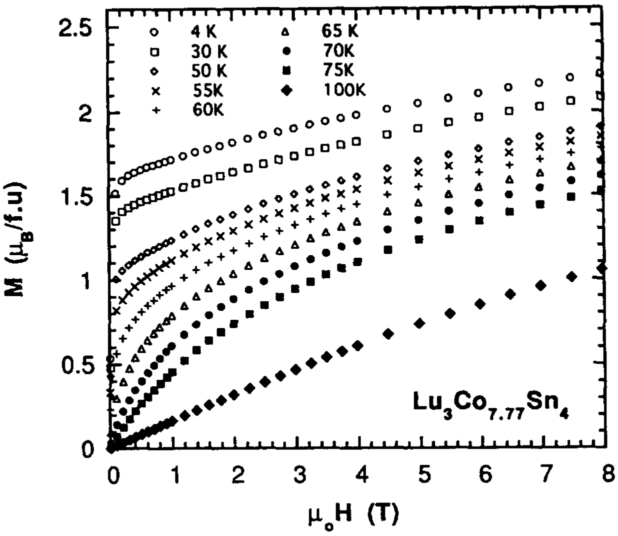

Fig. 2. Isothermal variations of magnetisation for the $Lu_3Co_{7.77}Sn_4$ compound.

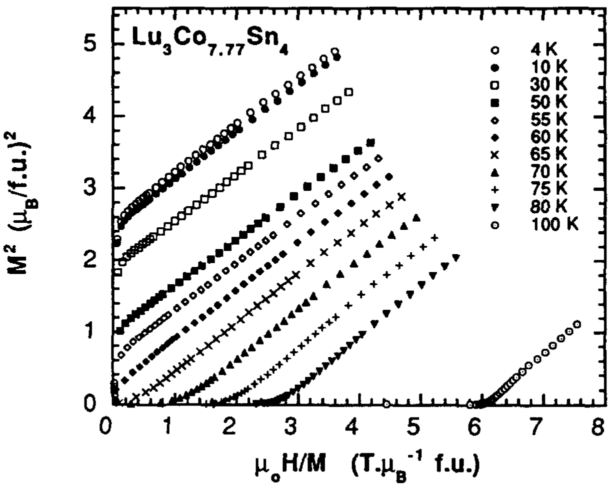

Fig. 3. Arrott plots for $Lu_3Co_{7.77}Sn_4$.

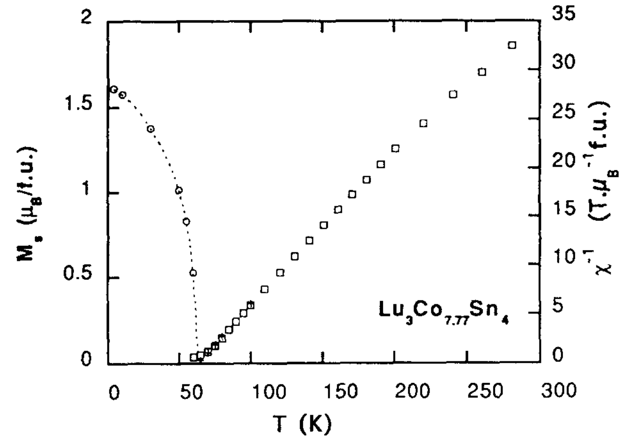

Fig. 4. Thermal dependence of the spontaneous magnetisation and reciprocal susceptibility of $Lu_3Co_{7.77}Sn_4$.

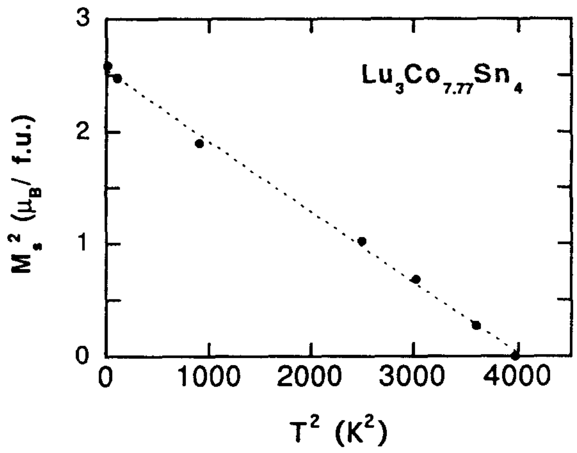

Fig. 5. Square of the spontaneous magnetisation as a function of T^2.

ered as individual excitations. The field dependence of magnetisation is then given by

$$\frac{M(H,T)^3}{M(0,0)^3} - \frac{M(H,T)}{M(0,0)}\left[1-\frac{T^2}{T_c^2}\right] = \frac{2\chi_0 H}{M(0,0)} \qquad (1)$$

which leads to:

$$M(H,T)^2 = M(0,0)^2\left[1-\frac{T^2}{T_c^2}\right] + \frac{2\chi_0 H}{M(H,T)} \qquad (2)$$

This expression shows that the Arrott plots must be parallel straight lines, and that the magnetisation increases with the field and does not reach saturation. The deduced thermal variation of the spontaneous magnetisation is then:

$$M^2(0,T) = M^2(0,0)\left[1-\frac{T^2}{T_c^2}\right] \qquad (3)$$

implying a linear dependence of $M^2(0, T)$ vs. T^2, as observed in the compound under investigation.

In the paramagnetic region, the reciprocal susceptibility follows rather well the linear Curie–Weiss law, at least below 200 K. The effective moment reaches 1.86 μ_B/Co, a value much larger than that corresponding to the low temperature spontaneous magnetization (0.19 μ_B/Co). In itinerant systems these moments are usually written as $\mu_B[q_c(q_c+2)]^{1/2}$ and $\mu_B q_s$ respectively [7,8]; q_c and q_s represent the number of carriers in both cases. In experimental systems, the ratio q_c/q_s ranges from a value a little larger than unity in pure Ni to almost ten. It characterises the degree of itineracy of a system and the nature of the spin fluctuations. In $Lu_3Co_{7.77}Sn_4$ one has $q_c/q_s \approx 5.5$, representing a value slightly larger than that of $ZrZn_2$ [9] which is the archetype of the VWIF behaviour. In this latter compound, polarized neutron diffraction experiments have shown than the magnetism is extremely diffuse [10], whereas in the YNi_3 very weak itinerant ferromagnet [11], the magnetism is localised on the Ni sites. This difference in localisation of magnetism in these materials arises from the difference of the band structures near the Fermi level. The Ni 3d band is almost filled, so the states responsible for magnetism have a localised antibonding character. In contrast, in $ZrZn_2$ the Zr-3d band is almost empty, so magnetic states have a delocalised bonding character [12]. In $Lu_3Co_{7.77}Sn_4$ the 3d band is almost filled and one can expect that magnetism is localised on Co sites in this itinerant system.

It can be speculated that mainly Co1 and Co4 atoms are responsible for the onset of ferromagnetism in these stannides. Indeed they form tetrahedral groups (Co4)3Co1 which are mutually connected alternatively by basal faces (Co4)3 or by tops (Co1) forming chains parallel to the *z* axis. The interatomic distances between Co1–Co4 atoms in these groups are markedly small, which could be the origin of the ferromagnetic interactions.

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