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Structure and magnetic properties of $CeCo_3Ga_2$

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Abstract

The compounds $CeCo_{5-x}Ga_x$ have been studied by X-ray diffraction and magnetic measurements. It is shown that ferromagnetic order disappears for $x \geq 2$. The absence of magnetic ordering in $CeCo_3Ga_2$ was confirmed by neutron diffraction. A structure determination made on the basis of the neutron data for $CeCo_3Ga_2$ basically confirmed the YCo_3Ga_2 structure type (hP18) but revealed a different distribution of Co and Ga over the three non-rare earth sites.

1. Introduction

Rare earth compounds of the type RCo_3Ga_2 have been reported [1] to crystallize with the hexagonal YCo_3Ga_2 structure (hP18), comprising two rare earth sites, two Co sites and one Ga site. The YCo_3Ga_2 structure is related to the $CaCu_6$ type structure of the compound YCo_5. It results after substituting Ga atoms into only one of the two Co sites present in YCo_5, followed by some rearrangement of the atoms to comply with the larger size of the Ga atoms at the Co positions [1]. In a later report of the crystallographic and magnetic properties of RCo_3Ga_2 compounds [2], X-ray diffraction evidence was presented that is in conflict with the YCo_3Ga_2 structure type mentioned above. In order to clarify this situation we have studied the compound $CeCo_3Ga_2$ by neutron diffraction.

A further purpose of the present investigation was to study the magnetic properties of the compound $CeCo_3Ga_2$, in view of the considerable magnetic hardness found in compounds YCo_3Ga_2 and $TbCo_3Ga_2$ for YCo_3Ga_2 when Ce is in the trivalent state.

2. Experimental details

The samples $CeCo_{5-x}Ga_x$ were prepared by arc melting from starting materials of at least 99.9% purity. The samples were wrapped into Ta foil and annealed inside evacuated quartz tubes at 800 °C for 3 weeks. In several cases the annealing treatment was also performed at 1000 °C, which led to virtually the same results. X-ray diffraction was performed with a Philips X-ray diffractometer type PW 1800/10.

Magnetic measurements were made on free powder particles. Measurements below room temperature were made on a SQUID magnetometer. For higher temperatures we used a home-built magnetometer based on the Faraday principle. Neutron diffraction experiments were made on $CeCo_3Ga_2$ at 120 K and 1.3 K. The data were collected with the DMC (double axis multicounter diffractometer) at the Reactor Saphir, Würenlingen, 1.7037 Å, using the high intensity mode. The step increment of the diffraction angle 2θ was 0.1°. The data were corrected for absorption and evaluated by the FULLPROF program [3] using scattering lengths for Ce, Co and Ga as reported in ref. 4.

3. Experimental results

3.1. X-ray diffraction

Samples of the composition $CeCo_{5-x}Ga_x$ with $x = 0$, 0.5, 1.0, 1.5, 2.0 and 3.0 were investigated by X-ray diffraction. The X-ray diagrams of the samples with $x = 0$, 0.5, 1.0 and 1.5 showed that the corresponding compounds had crystallized in the hexagonal $CaCu_5$-type structure. The X-ray diagram of $CeCo_3Ga_2$ was composed of reflections similar to those of the $CaCu_5$ type found for $x \leq 1.5$ but showed additional lines, some of which had roughly the same intensity as the main lines of the $CaCu_5$ type pattern. All reflections of the $CeCo_3Ga_2$ diagram were indexed on the basis of the YCo_3Ga_2-type structure (hP18) described earlier by

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Fremy *et al.* [1]. A similar type of pattern was also observed in the X-ray diagram of the sample with $x=3.0$, although many other lines were present, indicating that the sample probably is not single phase. This sample was therefore excluded from magnetic measurements.

3.2. Magnetic measurements

Results of measurements of the temperature dependence of the magnetization are shown for several representative compounds in Fig. 1. The concentration dependence of the Curie temperature of the $CeCo_{5-x}Ga_x$ compounds is shown in Fig. 2 and the field dependence of the magnetization at 5 K is shown for several compounds in Fig. 3. It can be derived from the results shown in Figs. 1–3 that the $CeCo_{5-x}Ga_x$ compounds are ferromagnetic only when $x \leq 1.5$.

3.3. Neutron diffraction

The neutron diffraction pattern collected at 120 K is shown in Fig. 4 (top part). The refined parameters given in Table 1 confirm the YCo_3Ga_2 type of structure [1], except for a different distribution of the Co and Ga atoms over the available non-rare earth sites [1]. The *R*-factor values are satisfactory and indicate no other significant deviation from the basic YCo_3Ga_2 structure.

The low temperature data taken at 1.3 K do not present any changes of the intensities of the nuclear contributions as would have been expected for prevailing ferromagnetic ordering. Confirmation of the absence of magnetic ordering was also obtained from the difference diagram 1.2–120 K. The low-angle peaks 100, 110, 001, 200, 101, 111 which are not overlapping with strong nuclear reflections would have been particularly sensitive to the presence of ferromagnetic contributions but they were found to show no significant enhancement from the background (Fig. 5).

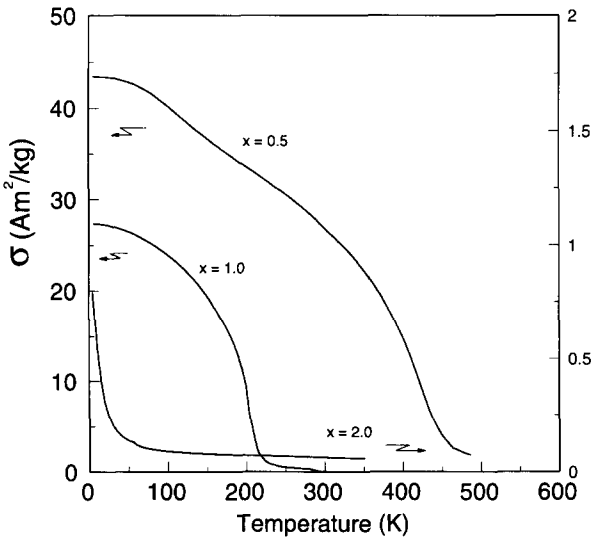

Fig. 1. Temperature dependence of the magnetization of several field-cooled (2.0 T) samples of the type $CeCo_{5-x}Ga_x$ measured with $\mu_0 H=0.1$ T.

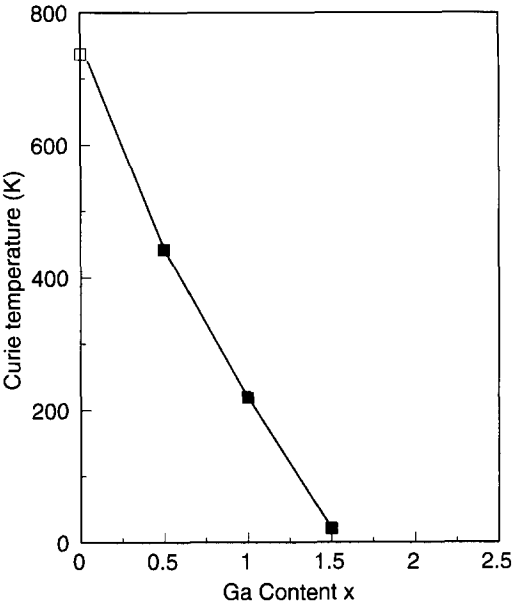

Fig. 2. Concentration dependence of the Curie temperature in the series $CeCo_{5-x}Ga_x$. The value plotted for $x=0$ was taken from ref. 6.

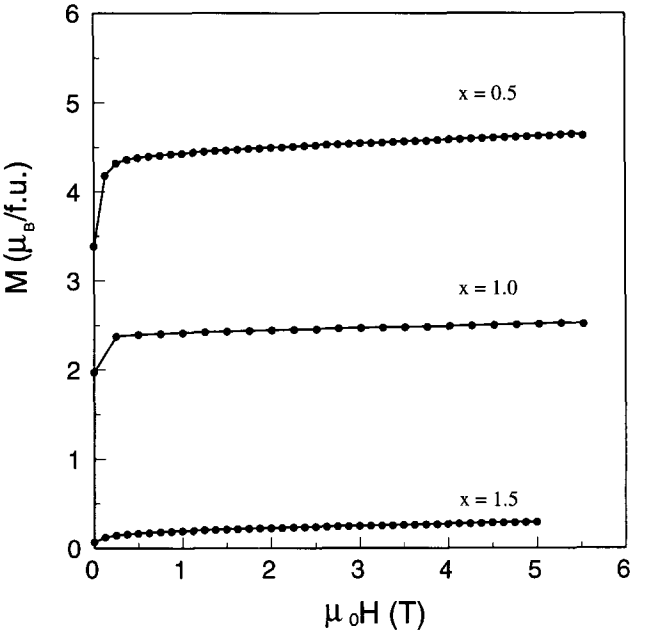

Fig. 3. Field dependence of the magnetization at 5 K for several compounds of the type $CeCo_{5-x}Ga_x$.

4. Discussion

It has been shown already by Fremy *et al.* [1] that substitution of Ga for Co in $CaCu_5$-type RCo_5 compounds leads to a new type of ternary compound around

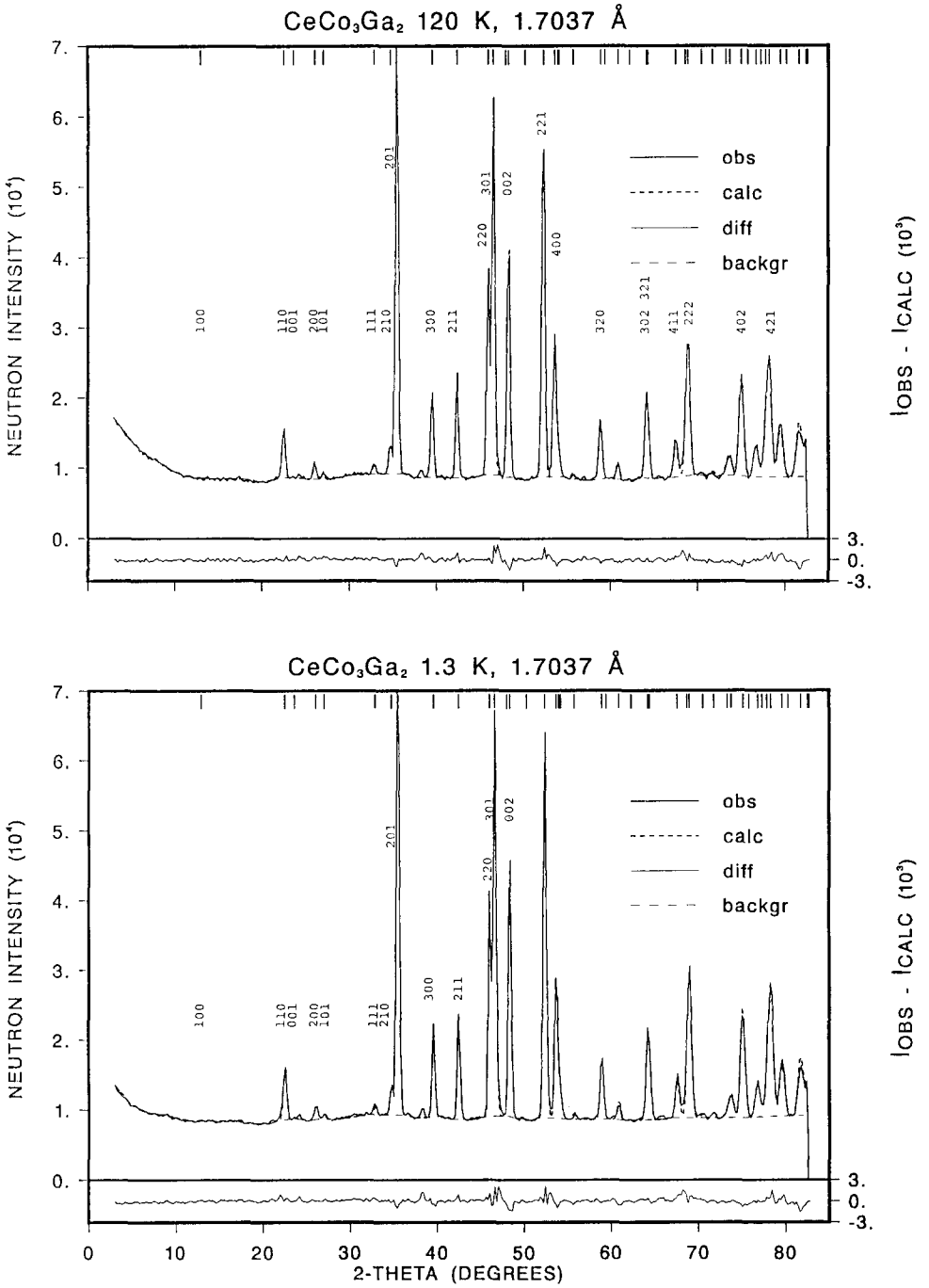

Fig. 4. Neutron diffraction diagram of $CeCo_3Ga_2$ at 120 K (top part) and 1.3 K (bottom part).

the formula composition RCo_3Ga_2. The crystal structure of these ternary compounds is related to the $CaCu_5$ type. It can be described by preferential occupation of one of the two Co sites in RCo_5 by Ga and a shift of one-third of the R atoms along the c axis into the $z=\frac{1}{2}$ plane. In standard X-ray diffraction the occurrence of this structure type (YCo_3Ga_2-type) is easily recognized by the appearance of two strong lines (201 and 211) in the X-ray pattern which otherwise bears a close resemblance to that of the $CaCu_5$ parent pattern.

Later on Felner *et al.* [5] investigated the structure and magnetic properties of the compounds $TbCo_3Ga_2$ and $Y_2Co_3Ga_2$. The authors showed that $TbCo_3Ga_2$ gives rise to a new structure type derived from the $CaCu_5$ type but did not present a structure determination. Inspection of their X-ray data indicates that the underlying crystal structure is the same as the YCo_3Ga_2 type described by Fremy *et al.* [1]. Evidently the authors were not aware of the latter structure determination.

TABLE 1. Refined structural parameters of the $CeCo_3Ga_2$ compound (a) in the paramagnetic state at 120 K (b) in the magnetically ordered state at 1.3 K. Space group *P6/mmm*

Atom	Site	Occup.	Temperature					
			1.3 K			120 K		
			x	*y*	*z*	*x*	*y*	*z*
Ce(1)	1a	1.0	0.0	0.0	0.5	0.0	0.0	0.5
Ce(2)	2c	1.0	0.3333	0.6666	0.0	0.3333	0.6666	0.0
Co(1)	6m	1.0	0.1801(8)	0.3529(8)	0.5	0.1803(7)	0.3533(8)	0.5
Co(2)	6j	0.5	0.2810(3)	0.0	0.0	0.2810(3)	0.0	0.0
Ga(1)	6j	0.5	0.2810(3)	0.0	0.0	0.2810(3)	0.0	0.0
Ga(2)	3g	1.0	0.5	0.0	0.5	0.5	0.0	0.5
a (nm), *c* (nm)		0.87216(8)	0.41628(4)			0.87303(8)	0.41651(4)	
*B*of (nm^2)		0.0065(7)				0.0079(6)		
R_n(%), R_{wp}(%)		4.3	7.7			5.05	7.35	
R_{exp}(%)		1.9				2.9		

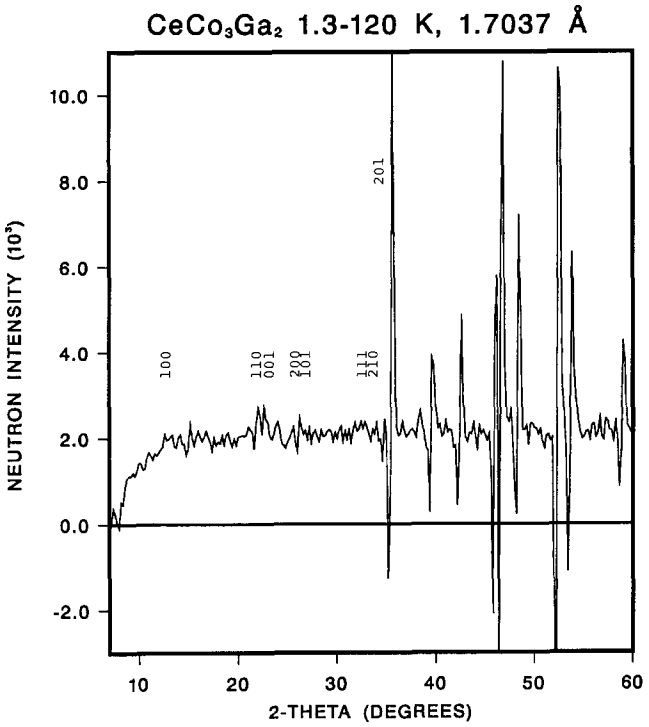

Fig. 5. Difference diagram obtained by subtracting the intensities of the 120 K neutron diagram from the 1.3 K diagram.

It is interesting to compare the distribution of Co and Ga atoms over the three available non-rare earth positions in the YCo_3Ga_2 structure type reported by Fremy *et al.* with that found in the present neutron diffraction study. In order to facilitate this comparison we have listed the site occupancies found in the two investigations in Table 2. In the structure determination of Fremy *et al.* (last column of Table 2) the Ga atoms strictly occupy a single site (6j), which corresponds to the 2c site of the original $CaCu_5$ type. In the present structure determination (third column of Table 2) the

TABLE 2. Occupancies according to results obtained in the course of the present investigation [p.i.] and according to results reported in ref. 1

Atom	Site	Occ. [p.i]	Occ. [1]
R(1)	1a	1.0	1.0
R(2)	2c	1.0	1.0
Co(1)	6m	1.0	1.0
Co(2)	6j	0.5	0.0
Ga(1)	6j	0.5	1.0
Co(3)	3g	0.0	1.0
Ga(2)	3g	1.0	0.0

Ga atoms are distributed over two sites, the 3g site being fully occupied by Ga atoms and the 6j site being half occupied. Further neutron experiments are planned in order to investigate how far the site occupancies depend on the nature of the R and T elements in RT_3Ga_2 compounds.

The structure and magnetic properties of RCo_3Ga_2 compounds were also studied by Routsi *et al.* [2]. These authors did not observe the strong 201 and 211 reflections characteristic of the YCo_3Ga_2 structure type. Their X-ray data indicate that the $CaCu_5$ structure has basically remained preserved, the Ga atoms substituting preferentially into the 3g site in the original $CaCu_5$ structure type, the characteristic shift in the YCo_3Ga_2-type of some of the R atoms along the *c* direction into the $z=\frac{1}{2}$ plane being absent. Although Routsi *et al.* used space group *P6/mmm* of the YCo_3Ga_2-type, their atomic position parameters correspond to the ideal positions in the $CaCu_5$ structure type and do not involve shifts of the R atoms. Based on the experimental X-ray data presented, it can be concluded therefore that the compounds RCo_3Ga_2 studied by Routsi *et al.* [2] have crystallized in a different crystal structure from the $CeCo_3Ga_2$ compound studied in the course of the

present investigation. This may explain the fact that our sample does not show magnetic ordering whereas Routsi *et al.* [2] report a magnetization of 0.47 μ_B/(f.u.)$^{-1}$ and a remanence of 1.7 Am^2 kg^{-1} at 5 K.

It is interesting, though, to compare the properties of $CeCo_3Ga_2$ with those of YCo_3Ga_2 when both compounds have crystallized in the same structure. The latter compound has been reported to have a magnetic ordering temperature of about 85 K, contrasting the absence of magnetic ordering in $CeCo_3Ga_2$. This result is most likely due to the predominantly tetravalent character of Ce and the concomitant stronger reduction of the Co moment upon compound formation.

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