Crystal and electronic structures of the new quaternary RCr_3Si_2C (R=Y, Gd–Tm, Lu, U) compounds

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A B S T R A C T

Nine new quaternary intermetallic RCr_3Si_2C (R=Y, Gd–Tm, Lu, U) compounds have been synthesized and characterized by both powder and single-crystal X-ray diffraction. These compounds crystallize in the hexagonal system with space group $P6/mmm$ and lattice parameters $a \sim 9$ Å and $c \sim 4$ Å. Single-crystal X-ray diffraction refinement evidences a new type-structure closely related to the YCo_3Ga_2-type. Electronic structure properties and crystal stability of real YCr_3Si_2C against hypothetical YCr_3Si_2 are discussed in view of the Korringa–Kohn–Rostoker calculations, accounting for models with different atomic occupancy on selected sites as well as emphasizing the role of carbon in stabilization of YCr_3Si_2C compound.

1. Introduction

The RCr_2Si_2 (R=Y, Sm, Gd–Lu) [1,2] and RCr_2Si_2C (R=Y, La–Nd, Sm, Gd–Er) [3–6] compounds crystallize in the tetragonal $ThCr_2Si_2$-type structure ($I4/mmm$) [7] and $CeCr_2Si_2C$-type structure ($P4/mmm$) [3], respectively. These structural types are both related to the $CeMg_2Si_2$-type ($P4/mmm$) [8]. Indeed, the $CeCr_2Si_2C$-type is a variant of the $CeMg_2Si_2$-type, where the $1b$ site is totally occupied by the carbon atoms, while the $ThCr_2Si_2$-type structure is related to the $CeMg_2Si_2$-type by a simple [1/2, 1/2, 0] translation of one "X–R–X" slab out of two. Thus, the $ThCr_2Si_2$ and the $CeMg_2Si_2$ structures differ only in the coordination of the transition metal, which is tetrahedral in $ThCr_2Si_2$ and rectangular in $CeMg_2Si_2$ [6].

The RCr_2Si_2 (R=Y, Sm, Tb–Lu) compounds exhibit strong antiferromagnetic properties ($T_N \geq 600$ K) due to a large magnetic moment on the chromium sublattice ($\sim 1.96 \mu_B$), whereas the rare-earth sublattice orders antiferromagnetically at very low temperature ($T < 5$ K) [6,9–11]. In contrast, the RCr_2Si_2C (R=Y, La–Nd, Sm, Gd–Er) compounds exhibit a ferromagnetic order on the rare-earth sublattice ($T_C \leq 35$ K), while the chromium sublattice seems to be none magnetically ordered [6,12–14]. Electronic structure calculations have shown that the quenching of the magnetic moment of

chromium and modification of the sign of the magnetic coupling R–R are due to the strong hybridization between d states on chromium atoms and p states on carbon atoms [6].

During investigations on RCr_2Si_2C (R=rare-earth) compounds, we have evidenced the new quaternary RCr_3Si_2C (with R=Y, Gd–Tm, Lu, U) intermetallic compounds. In this paper, we report on the crystal structure of these new compounds, investigated experimentally by powder and single-crystal X-ray diffraction and theoretically by electronic structure calculations.

2. Experimental methods

The RCr_3Si_2C (with R=Y, Gd–Tm, Lu and U) compounds have been synthesized starting from high purity elements (≥ 99.9 wt%). Pure elements have been melted in a water-cooled copper crucible using a high frequency induction furnace under pure argon atmosphere, without annealing after melting. The purity and chemical composition of each sample have been checked by microprobe analysis (Cameca SX 100) at the Service Commun de Microscopies Electroniques et de Microanalyses de l'Université de Lorraine.

Single crystals of YCr_3Si_2C have been extracted from the as-cast ingots and characterized at room temperature with a Nonius Kappa-CCD area detector X-ray diffractometer (Mo $K\alpha$, λ=0.71073 Å) at the Service Commun de Diffractométrie de l'Université de Lorraine. The conditions of data collection and structure refinements are gathered in Table 1. The refinements were conducted using the SHELX97 software [15].

The crystallographic structure and the presence of impurities in the polycrystalline samples have been checked by powder X-ray diffraction (Philips X'Pert Pro Diffractometer, Cu $K\alpha$). The analysis of the patterns has been performed by Rietveld profile refinement using the FULLPROF software [16,17].

3. Crystal structure determination

In order to precisely determine crystallographic structure of the new quaternary $R\mathrm{Cr_3Si_2C}$ compounds, $\mathrm{YCr_3Si_2C}$ sample has been studied by single-crystal X-ray diffraction.

Structure refinements indicate that $\mathrm{YCr_3Si_2C}$ crystallizes in a hexagonal unit cell with the space group $P6/mmm$ and the refined cell parameters $a=9.0334(1)$ Å and $c=3.9899(1)$ Å (Table 1). The $\mathrm{YCo_3Ga_2}$-type structure [18] is also known to crystallize in the space group $P6/mmm$ with cell parameters and chemical composition close to those determined for $\mathrm{YCr_3Si_2C}$. However, structure refinements performed with this model do not converge, while inversion of the crystallographic sites occupied by p-element (Si/Ga) and transition metal (Cr/Co) allow to obtain better refinements. Thus, the yttrium atoms occupy the 2d (1/3, 2/3, 1/2) and 1a (0, 0, 0) sites, the chromium atoms occupy the 6k ($\sim$0.28, 0, 1/2) and 3f (1/2, 0, 0) sites and the silicon atoms the 6l ($\sim$0.19, $\sim$0.38, 0) site (Table 2).

Refinements indicate no disorder between Cr and Si on the 6k, 3f and 6l sites and a full occupation of the 2d site by the Y atoms, while the 1a site is partially occupied. Fourier maps also evidence

electron density around the (0, 0, $\sim$0.3) position corresponding to a partial occupation of a 2e site by the yttrium atoms. In so far as occupation of both 1a and 2e sites in the same unit cell is geometrically impossible, a statistical distribution of the Y atoms on the two sites (i.e. 1a and 2e) should be considered. Presence of few atoms of rare-earth localized between these two crystallographic sites is not completely excluded.

Due to the presence of heavy atoms (R, Cr, Si), the localization and occupation rate of the carbon atoms cannot be determined unambiguously by X-ray diffraction. However, the neutron scattering length of carbon ($b=+6.648$ fm) allows to distinguish this element among rare earth ($+7.07$ fm $\leq b \leq +8.61$ fm for Tm and U, respectively), chromium ($b=+3.635$ fm) and silicon ($b=+4.159$ fm) atoms. Thus, neutron powder diffraction measurements have been carried out on the D1B diffractometer (ILL, Grenoble, France). Rietveld refinements of neutron patterns indicate unambiguously the localization of the carbon atoms on the full filled 3g site.

The final single crystal X-ray diffraction refinements have been performed with the 3g site totally filled by carbon atoms and with 1a and 2e sites partially filled by yttrium atoms. The results of the refinement are gathered in Table 2, and lead to the chemical composition $\mathrm{Y_{0.96}Cr_3Si_2C}$. The yttrium sub-stoechiometry can be explained by a possible localization of rare-earth atoms between the 1a and 2e crystallographic sites, which is not taking into account in the refinements. This crystallographic structure has also been confirmed by single-crystal X-ray diffraction on $\mathrm{TmCr_3Si_2C}$ sample [19].

Representations of the crystal structure, considered without disorder on the lanthanide 1a and 2e sites, are shown in Fig. 1. Interatomic distances of $\mathrm{YCr_3Si_2C}$, gathered in Table 3, have been calculated from single-crystal refinement. Their relative evolutions have been calculated from the relation $\Delta_{ij}=(100[d_{ij}-(r_i+r_j)])/(r_i+r_j)$, where d_{ij} is the interatomic distance between atoms i and j, and r_i and r_j, the metallic radius of the corresponding atoms evaluated by Teatum et al. [20] (i.e. $r_Y=1.801$ Å, $r_{Cr}=1.360$ Å, $r_{Si}=1.319$ Å and $r_C=0.916$ Å). These calculations evidence three-dimensional stability of the crystallographic structure due to strong chemical bonds both in the atomic plane ($z=0$ and $z=1/2$) and between them (Figs. 2 and 3).

These calculations also evidence that the Si(6l)–C(3g) distances (3.1696 Å) are larger compared to the sum of the metallic radii ($\Delta=+41.8\%$), indicating no chemical bond between silicon and carbon atoms. On the contrary, the very short Cr(6k)–C(3g) and Cr(3f)–C(3g) distances (Table 3) indicate a partially covalent strong bonds between chromium (Cr(6k), Cr(3f)) and carbon atoms (Figs. 2 and 3). Thus, these crystallographic results indicate a greater affinity between carbon and chromium atoms than between carbon and silicon atoms. This difference of chemical affinity can be related with the inversion of the crystallographic sites occupied by p-element (Si/Ga) and transition metal (Cr/Co) compare to the $\mathrm{YCo_3Ga_2}$-type structure. These crystallographic results also suggest an important

Table 1
Summary of data collection and structure refinement conditions for $\mathrm{YCr_3Si_2C}$ compound at room temperature.

Structural formula	$\mathrm{Y_{0.96}Cr_3Si_2C}$
Molar mass (g mol^{-1})	309.80
Symmetry	Hexagonal
Space group	$P6/mmm$
a (Å)	9.0334(1)
c (Å)	3.9899(1)
V (Å^3)	281.965(8)
Z	3
ρ (g cm^{-3})	5.48
Radiation	Mo $K\alpha$
Monochromator	Graphite
θ range	3.03°–29.70°
Linear abs. Coeff. μ (mm^{-1})	23.41
Reflections collected	551
Reflections unique	199
F (000)	424
Number of parameters	19
Final R value (%)	2.89
S (Goodness of fit)	1.220

Table 2
Atomic coordinates, site occupancy and thermal parameters of $\mathrm{YCr_3Si_2C}$.

Site	Atom	x	y	z	m_j	U_{11}	U_{33}	U_{12}
$\mathrm{Y_{0.96}Cr_3Si_2C}$ ($R=2.89\%$)
2d	Y	1/3	2/3	1/2	1.0	$2U_{12}$	0.0048(5)	0.0024(2)
1a	Y	0	0	0	0.667(8)	$2U_{12}$	0.0256(17)	0.0025(4)
2e	Y	0	0	0.295(2)	0.112(3)	–	–	–
6k	Cr	0.28523(11)	0	1/2	1.0	0.0056(4)	0.0034(5)	0.0021(2)
3f	Cr	1/2	0	0	1.0	0.0046(5)	0.0030(7)	0.0019(3)
6l	Si	0.18717(11)	2x	0	1.0	0.0053(5)	0.0053(8)	0.0039(4)
3g	C	1/2	0	1/2	1.0	–	–	–

$T_j=\exp[-2\pi^2U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*]$ with $U_{22}=2U_{12}$ and $U_{13}=U_{23}=0$.