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# Crystal structure of new quaternary intermetallic compounds $R_2\text{MoSi}_2\text{C}$ ( $R = \text{Y, Gd}$ )

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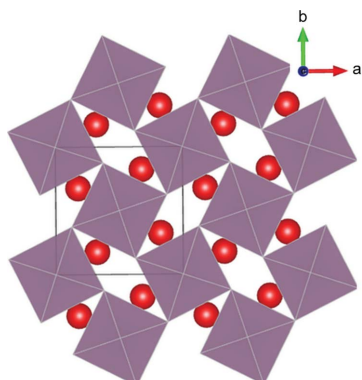
The discovery of novel quaternary intermetallic compounds  $R_2\text{MoSi}_2\text{C}$  ( $R = \text{Y, Gd}$ ) in the  $R\text{--Mo--Si--C}$  system is reported. Their crystal structure was investigated using single-crystal X-ray diffraction. It is shown that the  $\text{Y}_2\text{MoSi}_2\text{C}$  and  $\text{Gd}_2\text{MoSi}_2\text{C}$  compounds crystallize in the tetragonal space group  $P4/mbm$  (Pearson symbol tP12) with unit-cell parameters  $a = 6.9525(18) \text{ \AA}$ ,  $c = 4.1962(16) \text{ \AA}$ , and  $a = 6.9945(16) \text{ \AA}$ ,  $c = 4.2020(14) \text{ \AA}$ , respectively.

## 1. Introduction

Among solid materials, intermetallic compounds occupy a special place, characterized by great diversity in both their physical properties and crystal chemistry. Within the ternary intermetallics  $RT_2\text{Si}_2$  (where  $R$  is a rare earth metal and  $T$  is a transition metal), the chromium-based compounds were found to be stable for  $R = \text{Nd, Sm}$  and  $\text{Gd--Lu}$  (Rieger & Parthé, 1969; Dommann *et al.*, 1988; Dirken *et al.*, 1989; Prots' *et al.*, 1994; Morozkin, 2004) and exhibit strong antiferromagnetic behavior ( $T_N \geq 600 \text{ K}$ ) due to a large magnetic moment on the Cr sublattice ( $\sim 1.96 \mu_B$ ), whereas the lanthanide sublattice orders antiferromagnetically at very low temperatures ( $< 5 \text{ K}$ ) (Moze *et al.*, 2003; Janatová *et al.*, 2010). The quaternary  $R\text{Cr}_2\text{Si}_2\text{C}$  compounds (with  $R = \text{Y, La--Sm, Gd--Er}$ ) crystallize in the carbon-filled  $\text{CeMg}_2\text{Si}_2$ -type structure (space group  $P4/mmm$ ) (Tang *et al.*, 2000; Pohlkamp & Jeitschko, 2001; Janatová *et al.*, 2008; Ma *et al.*, 2022). These carbides exhibit ferromagnetic behavior on the lanthanide sublattice at low temperature for  $R = \text{Pr, Nd, Gd--Dy}$  while the Cr sublattice seems to be non-magnetically ordered unlike the magnetic behavior previously described for the  $R\text{Cr}_2\text{Si}_2$  compounds (Janatová *et al.*, 2008; Klosek *et al.*, 2008; Ma *et al.*, 2022). The magnetism of  $\text{CeCr}_2\text{Si}_2\text{C}$  remains controversial (Tang *et al.*, 2000; Klosek *et al.*, 2008; Mukherjee *et al.*, 2010; Wang *et al.*, 2023).

In this context, the  $R\text{--Mo--Si--C}$  quaternary equilibrium diagram represents an interesting system, demonstrating intermediate valence phenomena in the  $\text{CeMo}_2\text{Si}_2\text{C}$  compound and, more recently, superconductivity in its thorium-based parent compound (Paramanik *et al.*, 2013a,b; Liu *et al.*, 2021).

In our exploratory research to investigate the possible extension of the layered  $R\text{Mo}_2\text{Si}_2\text{C}$  (with  $R = \text{Y, Gd}$ ) family, we have unexpectedly discovered two new compounds  $\text{Y}_2\text{MoSi}_2\text{C}$  and  $\text{Gd}_2\text{MoSi}_2\text{C}$ . In the present paper, we report on their crystal structure.



**Table 1**  
Experimental details.

	Y <sub>2</sub> MoSi <sub>2</sub> C	Gd <sub>2</sub> MoSi <sub>2</sub> C
Crystal data		
$M_r$	341.91	478.44
Crystal system, space group	Tetragonal, $P4/mbm$ (No. 127)	Tetragonal, $P4/mbm$ (No. 127)
Phase prototype	Y <sub>2</sub> MoSi <sub>2</sub> C (tP12)	Y <sub>2</sub> MoSi <sub>2</sub> C (tP12)
Temperature (K)	293	293
$a, c$ (Å)	6.9525 (18), 4.1962 (16)	6.9945 (16), 4.2020 (14)
$V$ (Å <sup>3</sup> )	202.83 (13)	205.57 (12)
$Z$	2	2
$\rho$ (g cm <sup>-3</sup> )	5.642	7.732
Radiation type	Mo $K\alpha$	Mo $K\alpha$
$\theta_{\max}$ (°)	36.08	35.88
$F(000)$	308	408
$\mu$ (mm <sup>-1</sup> )	31.78	35.25
Crystal size (mm)	0.03 × 0.02 × 0.02	0.03 × 0.02 × 0.02
Data collection		
Diffractometer	Bruker APEX II QUAZAR CCD	Bruker APEX II QUAZAR CCD
Absorption correction	Multi-scan	Multi-scan
$T_{\min}, T_{\max}$	0.7, 0.9	0.7, 0.9
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	2125, 281, 251	1359, 287, 274
$R_{\text{int}}$	0.052	0.039
$(\sin \theta/\lambda)_{\max}$ (Å <sup>-1</sup> )	0.829	0.824
Refinement		
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.026, 0.059, 1.19	0.019, 0.038, 1.13
Final $R1$ ( $I > 4\sigma$ )	0.0258	0.0198
Final $wR2$ ( $I > 4\sigma$ )	0.059	0.0733
No. of independent reflections	281	287
No. of observed reflections, restraints, parameters	251, 0, 16	274, 0, 14
$\Delta\rho_{\max}, \Delta\rho_{\min}$ (e Å <sup>-3</sup> )	1.00, -2.23	1.24, -1.66

## 2. Experimental

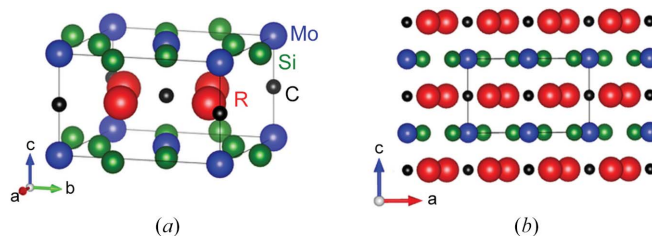
Synthesis in a high-frequency induction furnace was undertaken to obtain the quaternary polycrystalline compounds  $RMo_2Si_2C$  (with  $R = Y, Gd$ ). High-purity starting elements ( $\geq 99.9\%$ ) were used. Stoichiometric amounts of elements, for a total sample mass of about 5 g, were melted under a highly purified argon gas atmosphere. Pieces of Y, Gd and Mo were used while Si and C powders were introduced as pellets. Under the synthesis conditions used, the  $YMo_2Si_2C$  and  $GdMo_2Si_2C$  compounds could not be obtained.

However, the presence of single crystals was detected when observing the as-cast ingots, and then they were subsequently extracted. Very small single crystals were selected under a binocular microscope, glued to MiTeGen MicroLoops and then mounted on a four-circle diffractometer. Data acquisition was performed at 300 K using a Bruker APEX-II Quazar CCD diffractometer equipped with a CCD detector using Mo  $K\alpha$  radiation ( $\lambda = 0.71073$  Å). Cell refinement and data reduction were carried out using the *APEX2* (Bruker, 2006) software. The structure solution was obtained using direct methods and refined using full-matrix least-squares techniques with *Sir97* (Altomare *et al.*, 1999) and *SHELXL2018/3-97* (Sheldrick,

2015) software, respectively, implemented by employing the *WinGX* suite (Farrugia, 2012). Semi-empirical absorption correction using *SADABS* (Bruker, 2004) was applied to the data. The illustrations were made using *VESTA* (Momma & Izumi, 2011).

## 3. Crystal structure determination and discussion

The crystal structure was determined in the tetragonal lattice system in centrosymmetric space group  $P4/mbm$  (No. 127). The refinement parameters and main crystallographic data are



**Figure 1**  
(a) 3D-representation and (b) projection along the  $b$  axis of the crystal structure of  $R_2MoSi_2C$  compounds.

**Table 2**

Atomic coordinates, site occupancy ( $m_j$ ) and atomic displacement parameters of  $Y_2MoSi_2C$  at room temperature.

$$\bar{T}_j = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]; U_{22} = 2U_{12}; U_{13} = U_{23} = 0.$$

Site	Atom	$x/a$	$y/b$	$z/c$	$m_j$	$U_{11}$	$U_{33}$	$U_{12}$	$U_{eq}$
4h	Y	0.17653 (5)	$x + \frac{1}{2}$	$\frac{1}{2}$	1.0	0.00328 (19)	0.006 (1)	-0.00053 (16)	0.00417 (15)
2a	Mo	0	0	0	1.0	0.0021 (2)	0.0117 (3)	-	0.0053 (2)
4g	Si	0.62546 (16)	$x + \frac{1}{2}$	0	1.0	0.0046 (5)	0.0059 (7)	-0.0006 (5)	0.0050 (3)
2b	C	0	0	$\frac{1}{2}$	1.0	0.008 (2)	0.012 (4)	-	0.009 (2)

**Table 3**

Atomic coordinates, site occupancy ( $m_j$ ) and atomic displacement parameters of  $Gd_2MoSi_2C$  at room temperature.

$$\bar{T}_j = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]; U_{22} = 2U_{12}; U_{13} = U_{23} = 0.$$

Site	Atom	$x/a$	$y/b$	$z/c$	$m_j$	$U_{11}$	$U_{33}$	$U_{12}$	$U_{eq}$
4h	Gd	0.17668 (3)	$x + \frac{1}{2}$	$\frac{1}{2}$	1.0	0.00396 (11)	0.00376 (13)	-0.00033 (9)	0.00390 (9)
2a	Mo	0	0	0	1.0	0.0043 (2)	0.0055 (3)	-	0.00472 (14)
4g	Si	0.62525 (21)	$x + \frac{1}{2}$	0	1.0	0.0050 (4)	0.0048 (7)	-0.0010 (6)	0.0049 (3)
2b	C	0	0	$\frac{1}{2}$	1.0	0.018 (19)	0.005 (3)	-	0.0028 (13)

summarized in Table 1. The fractional atomic coordinates, site occupancy and displacement parameters are given in Tables 2 and 3. A perspective representation of the unit cell is depicted in Fig. 1(a) and a projection along the  $b$  axis is shown in Fig. 1(b). In this structure, all atoms occupy single crystallographic sites (Tables 2 and 3). The  $R$  atoms reside on the  $4h$  site with the point symmetry  $m.2m$ , generated by  $(x, x + \frac{1}{2}, \frac{1}{2})$ . The Mo and C atoms occupy the  $2a$  (0, 0, 0) and  $2b$  (0, 0,  $\frac{1}{2}$ ) Wyckoff positions, respectively, with an axial symmetry  $4/m$ . The silicon atoms are located on the  $4g$  crystal position with the point symmetry  $m.2m$ , generated by  $(x, x + \frac{1}{2}, 0)$ . The tetragonal unit cell consists of two formula units, and altogether it contains 12 atoms. This structure can be described as a C-filled variant of the  $U_3Si_2$  type (Zachariasen, 1948), more precisely it belongs to C-filled  $Mo_2FeB_2$ -type (Lukachuk & Pöttgen, 2003) with Y and Gd on the U  $4h$  site, molybdenum on the  $2a$  one and silicon on the silicon  $4g$  site.

This tetragonal structure is characterized by the stacking of alternating  $R_2C$  and  $MoSi_2$  square planes along the [001] direction.

Interatomic distances between atoms considered as nearest neighbors are gathered in Tables 4 and 5 for  $Y_2MoSi_2C$  and  $Gd_2MoSi_2C$ , respectively. They have been calculated from single-crystal refinement of the two new quaternary carbides. Their relative evolutions have been evaluated from the relationship:

$$\Delta_{ij} = \left(100[d_{ij} - (r_i + r_j)]\right)/(r_i + r_j) \quad (1)$$

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 (Teatum *et al.*, 1972; Venturini, 1989).

The results of these calculations show, for both compounds, short Mo–C distances ( $\Delta_{Mo-C} = -9.4\%$  in  $YMo_2Si_2C$  and  $-9.3\%$  in  $Gd_2MoSi_2C$ ). Short bonds between rare earth and silicon atoms ( $\Delta_{Y-Si} = -7.1\%$  and  $\Delta_{Gd-Si} = -7.6\%$ ) and rare earth and carbon atoms ( $\Delta_{Y-C} = -4.3\%$  and  $\Delta_{Gd-C} = -5.5\%$ ) are also present.

**Table 4**

Interatomic distances and their relative evolutions in  $Y_2MoSi_2C$ .

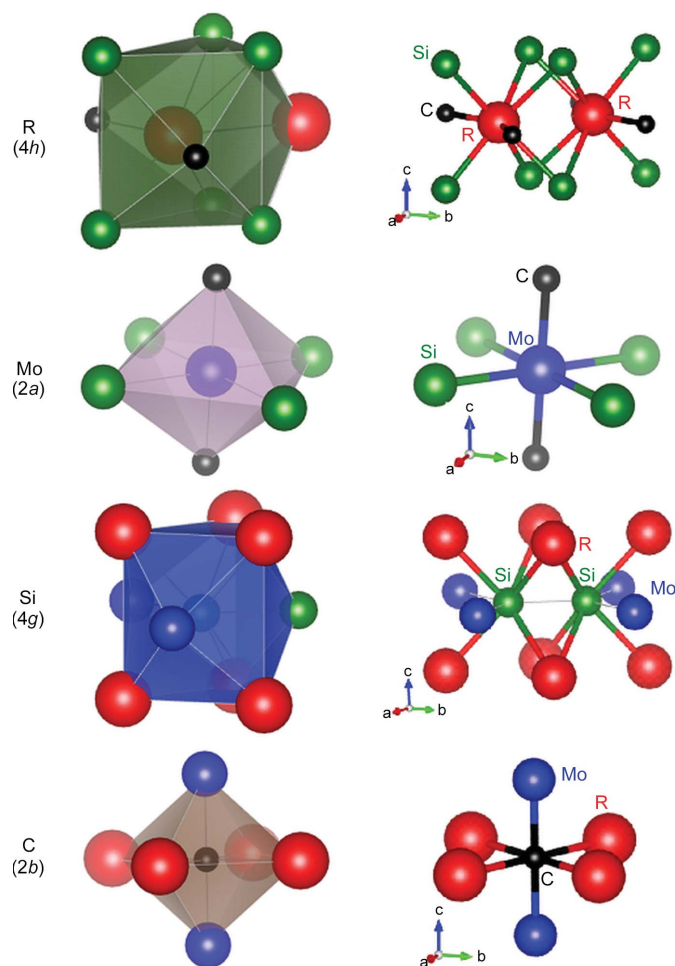
		$d_{inter}$ (Å)	$\Delta$ (%)
Y (4h)	4 Y	3.616 (2)	+2.6
	1 Y	3.463 (1)	-1.7
	4 Mo	3.3115 (7)	+4.7
	2 Si	2.8622 (13)	-7.1
	4 Si	2.9894 (10)	-3.0
	2 C	2.5620 (7)	-4.3
Mo (2a)	6 Y	3.3115 (7)	+4.7
	4 Si	2.7462 (10)	+1.0
	2 C	2.0981 (8)	-9.4
Si (4g)	4 Y	2.9894 (10)	-3.0
	2 Y	2.8622 (13)	-7.1
	2 Mo	2.7462 (10)	+1.0
	1 Si	2.4672 (33)	-6.5
C (2b)	4 Y	2.5620 (7)	-4.3
	2 Mo	2.0981 (8)	-9.4

**Table 5**

Interatomic distances and their relative evolutions in  $Gd_2MoSi_2C$ .

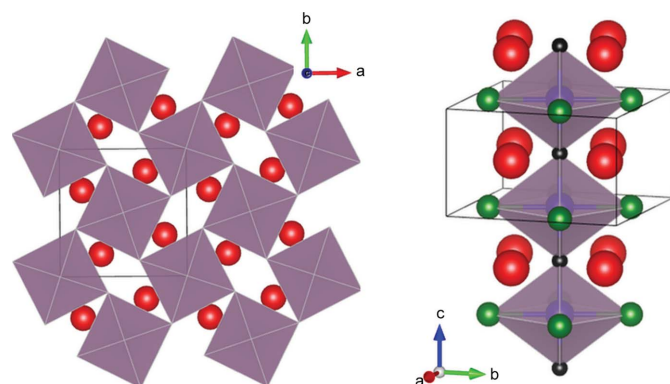
		$d_{inter}$ (Å)	$\Delta$ (%)
Gd (4h)	4 Gd	3.645 (2)	+1.8
	1 Gd	3.495 (1)	-2.4
	4 Mo	3.3250 (7)	+4.2
	2 Si	2.8748 (14)	-7.6
	4 Si	2.9994 (10)	-3.6
	2 C	2.5771 (6)	-5.5
Mo (2a)	6 Gd	3.3250 (7)	+4.2
	4 Si	2.7650 (10)	+1.7
	2 C	2.1010 (7)	-9.3
Si (4g)	4 Gd	2.9994 (10)	-3.6
	2 Gd	2.8748 (14)	-7.6
	2 Mo	2.7650 (10)	+1.7
	1 Si	2.472 (4)	-6.3
C (2b)	4 Gd	2.5771 (6)	-5.5
	2 Mo	2.1010 (7)	-9.3

The coordination polyhedra of each atom were established based on the shortest interatomic distances, and their relative evolutions were determined from single-crystal refinements.



**Figure 2**  
Coordination polyhedra in the  $R_2MoSi_2C$  compounds.

Two types of polyhedra describe the structure: tricapped deformed trigonal prisms and deformed octahedra (Fig. 2). The  $R$  atom is located at the center of a deformed trigonal prism of Si atoms, tricapped by two C atoms and one  $R$  atom. The deformed trigonal prism around Si is formed by six  $R$  atoms and is tricapped by two Mo atoms and one Si atom. The Mo atom is localized at the center of a deformed octahedron,



**Figure 3**  
View of the chain of  $MoSi_4C_2$  octahedra along the  $c$  axis.

with a distorted silicon square plane and two C atoms at the axial positions. Finally, the C atoms are positioned at the center of irregular octahedra, composed of  $R$  atoms in square planes and two Mo atoms at the top.

This new crystal structure can be described as chains of  $MoSi_4C_2$  octahedra along the  $c$  axis. These chains of octahedra form channels in which rare earth atoms are found (Fig. 3). The environment of molybdenum atoms is the same as that in the quaternary carbides  $RMo_2Si_2C$  structure (Dashjav *et al.*, 2006). This type of environment is also characteristic for chromium both in the  $RCr_2Si_2C$  and  $RCr_3Si_2C$  compounds (Klosek *et al.*, 2008; Lemoine *et al.*, 2013). All these results show that the stability of the novel structure is mainly based on the existence of strong bonds between Mo and C atoms like in the  $RMo_2Si_2C$  compounds without forgetting the  $R-Si$  and  $R-C$  bonds.

#### 4. Conclusion

Novel intermetallic compounds,  $Y_2MoSi_2C$  and  $Gd_2MoSi_2C$ , have been discovered during a survey of the  $R-Mo-Si-C$  phase diagram. Single-crystal X-ray diffraction analyses revealed the crystal structure parameters of a tetragonal cell with space group  $P4/mbm$ .

Further studies are planned in order to examine both the magnetic behavior of these new quaternary carbides and the existence of this new intermetallic phase with the other rare earth elements.

#### Conflict of interest

The authors declare no competing interests.

#### Data availability

The authors confirm that the data supporting the findings of this study are available within the article and its supplementary materials.

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