



Resonant X-ray diffraction study and electronic structure calculations of three Mo–Ru–Si ternary phases

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ABSTRACT

Resonant X-ray diffraction experiments at the Mo K-edge have been performed to study three ternary phases of the Mo–Ru–Si system with compositions $\text{Mo}_{58}\text{Ru}_{32}\text{Si}_{10}$ (σ -phase, CrFe type), $\text{Mo}_{40}\text{Ru}_{40}\text{Si}_{20}$ (χ -phase, αMn type) and $\text{Mo}_{26}\text{Ru}_{45}\text{Si}_{29}$ (β -phase) with the aim of increasing the scattering contrast between Ru and Mo. Multi-pattern Rietveld refinements allowed localizing the metallic elements on the different crystallographic sites of these structures. Chemical disorder was detected in all three investigated phases and the distribution of the elements was analyzed as a function of the atomic coordination and site volume. The two Frank–Kasper phases, σ and χ , are two phases showing the more pronounced atomic mixing with a tendency for Mo to prefer high coordination number (CN) sites while Si is excluded from these sites. The β -phase presents complete ordering of silicon on the sites with the smallest volumes. The total energy calculations, using the Korringa–Kohn–Rostoker method with the coherent potential approximation, were performed for different substitutional configurations of these three phases. The computed negative values of the formation energy support the experimental findings showing that Si prefers the crystallographic sites with the lowest CN. On the contrary, putting Si atoms in high CN crystallographic sites leads to substantial increase of the total energy and positive value of the formation energy. Moreover, several features of the density of states calculated for the most stable models are discussed.

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1. Introduction

Five ternary phases called σ , χ , β , ε and α (with increasing silicon content) have been identified in the isothermal section at 1673 K of the Mo–Ru–Si phase diagram and the main crystallographic features of these phases have already been presented [1]. The σ -, χ -, and α -phases were found to crystallize with known structure types. The structure of the β -phase was determined *ab-initio* from powder diffraction [2]. Up to now, the structure of the ε -phase remains unknown.

The σ -phase (structure type FeCr, space group $P4_2/mmm$, No. 136, 30 atoms per unit cell) is a common intermetallic compound in transition metal systems, pertaining to the group of Frank–Kasper phases. Its crystal structure and properties have been recently reviewed [3], with particular emphasis on its ability to accept extremely wide homogeneity ranges and to accommodate non-

stoichiometry on the five non-equivalent sites of its crystal structure (labeled M1–M5). The Mo–Ru–Si σ phase is a ternary extension of the binary Mo–Ru σ phase [4]. χ -phase (structure type αMn or $\text{Ti}_5\text{Re}_{24}$ or $\text{Mg}_{17}\text{Al}_{12}$, space group $I-43m$, No. 217, 58 atoms per unit cell) is another common Frank–Kasper phase which contains four crystallographic sites (labeled M1–M4) on which high substitutional disorder may occur. Its crystal structure properties have also recently been reviewed [3].

The β -phase $\text{Mo}_5\text{Ru}_8\text{Si}_5$ (space group $P4/mmm$, No. 123) is less common and has been identified, to our knowledge, only in the Mo–Ru–Si system [2]. The unit cell contains 18 atoms distributed among the six crystallographic sites (labeled M1–M6). Our earlier analysis from synchrotron radiation diffraction data has indicated that silicon atoms are ordered on two sites, M5 and M6. The distribution of Mo and Ru among the four other sites, M1–M4, has not been satisfactorily determined. Moreover, electronic structure calculations using Korringa–Kohn–Rostoker method with the coherent potential approximation (KKR-CPA) gave preliminary predictions [2], based on the analysis of the electronic structure features near the Fermi level as well as total energy preference, that

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Table 1
Summary of the refined parameters for the σ -, χ - and β -phases.

	σ	χ	β
EPMA comp.	Mo ₅₈ Ru ₃₂ Si ₁₀	Mo ₄₀ Ru ₄₀ Si ₂₀	Mo ₂₆ Ru ₄₅ Si ₂₉
Formula unit	Mo _{17.4} Ru _{9.6} Si _{3.0}	Mo _{23.3} Ru _{23.3} Si _{11.2}	Mo _{5.0} Ru _{8.0} Si _{5.0}
SG	P4 ₂ /mnm	I-43m	P4/mmm
a(Å)	9.45706(1)	9.36568(2)/9.35636(2)	9.22112(3)
c(Å)	4.94420(1)		2.88723(1)
μ_r	0.62	0.75	1.26
2- θ range	2–88°	2–88°	2–88°
R _p 1	4.43	8.15	12.3
R _p 2	4.31	8.29	13.1
R _p 3	4.37	8.71	15.0
R _{wp} 1	5.45	12.4	17.5
R _{wp} 2	5.13	12.0	18.6
R _{wp} 3	5.36	12.3	21.5
R _{exp} 1	3.21	4.79	5.35
R _{exp} 2	2.75	5.26	4.97
R _{exp} 3	3.43	4.34	4.32
R _{i1}	3.99	10.7	11.2
R _{i2}	2.96	11.5	11.9
R _{i3}	2.62	10.2	15.3
R _{F1}	5.25	13.2	7.4
R _{F2}	3.10	11.8	8.2
R _{F3}	3.09	10.5	13.9
N _{obs1}	17186	14325	28650
N _{obs2}	17186	14325	28653
N _{obs3}	28648	14325	28650
N _{Ref1}	1532	1050	956
N _{Ref2}	1535	1042	953
N _{Ref3}	1145	953	909
Profile param.	7	8	7
Intens. param.	17	15	11

site 1d, named here M3, was randomly occupied by Ru and Mo atoms.

Due to the proximity of Mo and Ru in the Periodic Table, the X-ray scattering contrast between these two elements is very low and conventional X-ray diffraction patterns cannot deliver accurate information on the occupancy parameters of these atoms in the investigated structures. This problem has been already highlighted in our previous paper on the β -phase [2]. Neutron diffraction cannot help since the diffraction contrast between Mo and Ru is also very low with this technique. Additionally, site occupancies cannot be obtained from a single diffraction experiment when three elements possibly share different sites.

These two problems can be overcome by using multi-pattern resonant X-ray diffraction. The α -phase of the Mo–Ru–Si system has already been studied by this technique which has shown its ability to perform accurate refinement of the respective site occupancies of Mo, Ru and Si [5]. In addition, theoretical analysis of the crystal stability of the binary phases MSi (with $M = Nb - Rh$) and ternary $Ru_{1-x}Mo_xSi$ (α -phase) solid solution has been recently studied with the use of the KKR-CPA technique [5].

In the present work, the same approach has been used to analyze the σ , χ and β phases, that exhibit more complex crystallographic structures [1,2]. The distribution of the three elements in the different crystallographic sites is reported. Important features of the electronic structure which are presumably responsible for the crystal stability and the selective atomic occupancy of non-equivalent crystallographic sites (M1–M6) are enlightened.

2. Experimental and computational details

2.1. Sample preparation and chemical analysis

The ternary compounds have been obtained as polycrystalline materials by melting the elemental Mo, Ru and Si powders. The details of the syntheses and the chemical analysis of the samples

Table 2

(a–c): Total energy (per chemical formula) and formation energy (per atom) calculated for different crystallographic models of σ (Mo₂₀Ru₇Si₃ composition; S1–S4 models), χ (Mo₂₄Ru₂₄Si₁₀ composition; K1–K4 models) and β (Mo₅Ru₈Si₅ composition; B1–B4 models) phases from the KKR-CPA method. Below each table the sum of total energies of elemental solids for considered composition are given for comparison.

(a) The σ -phase: composition Mo ₂₀ Ru ₇ Si ₃								
Model	Crystallographic sites [CN]					Formation energy (kJ/mol)	Total energy (Ry)	
	M1 [12] (2a)	M2 [15] (4f)	M3 [14] (8i ₁)	M4 [12] (8i ₂)	M5 [14] (8j)			
S1	2 Si	4 Mo	8 Mo	7 Ru	8 Mo	–10.5	–222809,443	
S2	1 Ru 1 Si	4 Mo	8 Mo	6 Ru 2 Si	8 Mo	–5.25	–222809,314	
S3	1 Ru	4 Mo	8 Mo	5 Ru 3 Si	8 Mo	–6.6	–222809,353	
S4	1 Ru	1 Mo 3 Si	8 Mo	3 Mo 5 Ru	8 Mo	+30.3	–222808,523	
20 E _{Mo} (fcc) + 7 E _{Ru} (hcp) + 3 E _{Si} (diamond) = –222809,208 Ry								
(b) the χ -phase: composition Mo ₂₄ Ru ₂₄ Si ₁₀								
Model	Crystallographic sites [CN]				Formation energy (kJ/mol)	Total energy (Ry/f.u.)		
	Sites	M1 [13] (24g ₁)	M2 [16] (8c)	M3 [12] (24g ₂)			M4 [16] (2a)	
K1	7 Mo 5 Ru	4 Mo	7 Ru 5 Si	1 Mo	–3.9	–409563,862		
K2	7 Ru 5 Si	4 Mo	7 Mo 5 Ru	1 Mo	+42.0	–409561,94		
K3	12 Mo	4 Si	12 Ru	1 Si	+36.8	–409562,16		
K4	12 Ru	4 Si	12 Mo	1 Si	+45.9	–409561,76		
24 E _{Mo} (fcc) + 24 E _{Ru} (hcp) + 10 E _{Si} (diamond) = –409563,792 Ry.								
(c) the β -phase: composition Mo ₅ Ru ₈ Si ₅								
Model	Crystallographic sites [CN]						Formation energy (kJ/mol)	Total energy (Ry/f.u.)
	M1 [14] (4n)	M2 [14] (4j)	M3 [14] (1d)	M4 [13] (4m)	M5 [10] (1b)	M6 [11] (4k)		
B1	4 Ru	1 Mo 3 Ru	1 Ru	4 Mo	1 Si	4 Si	–35.4	–113643,283
B2	4 Ru	0.5 Mo 3.5 Ru	0.5 Mo 0.5 Ru	4 Mo	1 Si	4 Si	–40.7	–113643,361
B3	4 Si	4 Ru	1 Mo	4 Mo	1 Si	4 Ru	+98.5	–113641,454
B4	4 Ru	4 Si	1 Si	4 Mo	1 Mo	4 Ru	+130.0	–113641,025
5 E _{Mo} (fcc) + 8 E _{Ru} (hcp) + 5 E _{Si} (diamond) = –113642,802 Ry								

have already been reported [5]. The compositions of the σ and χ phases were chosen approximately in the middle of the stability domains [6], i.e. Mo₅₈Ru₃₂Si₁₀ (σ -phase) and Mo₄₀Ru₄₀Si₂₀ (χ -phase). For the β -phase, three samples with close compositions have been analyzed: Mo₂₅Ru_{47.2}Si_{27.7} (Mo_{4.5}Ru_{8.5}Si₅), Mo_{27.7}Ru_{44.4}Si_{27.7} (Mo₅Ru₈Si₅) and Mo_{26.3}Ru_{45.8}Si_{27.7} (Mo_{4.75}Ru_{8.25}Si₅). The samples have been analyzed by electron microprobe analysis (EPMA) and their single phase characters have been confirmed and their composition was closed to the nominal one.

2.2. Synchrotron measurements

The synchrotron data have been obtained at the ESRF, Grenoble, France, on the beamline ID31. Each sample, constituted of fine powder, was introduced in a Lindeman tube ($\Phi = 0.4$ mm) and measured with the Debye–Scherrer geometry. Resonant diffraction experiments have been performed at room temperature successively at the MoK edges +2.5 eV (0.619852(1) Å), –16.5 eV (0.620427(3) Å) and –400 eV (0.63248(2) Å). For each pattern, data were recorded in the 2θ range 2–88° (2θ) with an interval of 0.003° and a total counting time of 3 h. Details about detection, calibration of the wavelength and calculation of the dispersion coefficients f' and f'' of Mo and Ru have already been given [5].

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