Preparation and Characterization of Mo₃Si and Mo₅Si₃

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Crystals of Mo₃Si were grown from a melt using the travelling solvent method and crystals of Mo₅Si₃ were grown from the melt using the Czochralski growth method.

Mo₃Si was characterized by neutron single crystal diffractometry and Mo₅Si₃ by neutron powder diffraction methods. Mo₃Si is cubic, Pm3n (No. 223), a=4.897(1) Å. Shortest Mo–Mo distance is 2.449(1) Å. Mo₅Si₃ is tetragonal, I4/mcm (No. 140), a=9.650(2), c=4.911(1) Å. Shortest Mo–Mo distance is 2.456(2) Å.

A large number of intermetallic compounds with the nominal composition A₃B are isostructural with β-W and have the so-called A15 structure. This structure belongs to the space group Pm3n, and has the A-atoms in site 6c and the B-atoms in site 2a. However, a major fraction of these intermetallic compounds are not strictly stoichiometric but exist in broad composition ranges. Mo₃Si is one of the few A15 compounds that has the stoichiometric A₃B composition at room temperature according to the literature 1-4 concerning the binary phase diagrams of the corresponding A–B system. Most of the intermetallic A15 compounds melt incongruently and this is also the case for Mo₃Si. In a project concerning development of crystal growth methods for incongruently melting compounds large single crystals of Mo₃Si were obtained. As Mo₃Si belongs to the stoichiometric A15 compounds it was decided to characterize the compound using neutron diffraction techniques.

Mo₅Si₃ is one of the congruently melting compounds in the Mo–Si systems. This compound was prepared as well and characterized by neutron diffraction technique.

EXPERIMENTAL

Crystal growth of Mo₃Si. The following compounds can be found in a zone melted rod of the composition Mo₃Si: The first part of the specimen contains a polycrystalline core of Mo₃Si and Mo₅Si. The rest of the specimen is Mo₃Si and the frozen zone is a mixture of Mo₃Si and Mo. This shows without ambiguity that the phase diagram published for the Mo–Si system in Ref. 5 is in error. It demonstrates in addition that Mo₅Si₃ isostructural with W₅Si₃ 6 is formed instead of a compound with the composition Mo₅Si₂. The structure of that compound has not been confirmed. In Fig. 1 is shown a fraction of the Mo–Si phase diagram reproduced from literature data 1 and with Mo₅Si₃ as one of the solid phases. The hatched area represents a two phase temperature composition range where the melt is in equilibrium with solid Mo₃Si. Single crystals of Mo₃Si can be made by a modified floating zone growth procedure, the so-called travelling solvent method where the molten zone of solvent has the nominal composition Mo₃Si, indicated by an arrow, z, in Fig. 1. The feed rod and the grown crystal have the composition Mo₃Si. The volume of the molten zone of solvent must be kept

![Fig. 1. Fraction of the phase diagram of the Mo–Si system (data from Ref. 1).](image-url)
constant in the floating zone like growth procedure. The crystals of Mo₃Si were made in an ADL-MP crystal growth unit at an ambient He pressure of 2 MPa. With a typical growth rate of 1 mm h⁻¹ single crystals of Mo₃Si with a volume of up to 1 cm³ were obtained.

Crystal growth of Mo₃Si₃. As can be seen from the phase diagram Fig. 1, the compound Mo₃Si₃ melts congruently and a normal Czochralski growth technique can be used in preparation of single crystals of Mo₃Si₃. Crystals of volume of up to 1 cm³ were pulled from the melt kept in a cold crucible. The pulling rate was 1 mm h⁻¹ and an ambient He pressure of 1 MPa was used.

Diffraction experiments. X-Ray diffraction powder patterns of Mo₃Si and Mo₃Si₃ were recorded on a Guinier camera with silicon as an internal standard using CuKα radiation. From these measurements the following unit cell parameters were calculated: a_{Mo₃Si}=4.897(1) Å, a_{Mo₃Si₃}=9.650(2) Å, c_{Mo₃Si₃}=4.911(1) Å.

Mo₃Si was characterized by single crystal neutron diffractometry. A single crystal of dimensions 2×2×2 mm was cut from a large crystal of Mo₃Si using spark erosion and this crystal was used in measuring neutron intensities using a four-circle neutron diffractometer at Risø. Neutrons of 0.8 Å wave length were used, and the ω-2θ scan technique was applied. Two standard reflections were measured for each 50 reflections, and a total of 1496 reflections were measured in a half sphere out to sin θ/λ=1.16 Å⁻¹. After correction for absorption (μ=0.065 cm⁻¹) and data reduction, the number of reflections with I>3σ(I) was 154. However, 26 of these were weak and space group forbidden, but apparently present due to multiple scattering. These reflections were omitted in the structure factor calculations. The parameters refined and the values arrived at for these parameters are listed in Table 1. A list of observed and calculated structure factors is available on request.

The least-squares program LINUS₂ was used in the structure factor calculations with the scattering lengths 0.695 and 0.4149 (in units of 10⁻¹² cm), respectively, for molybdenum and silicon. Mo₃Si₃ was characterized by neutron diffraction powder methods. Powder patterns were measured at room temperature on the D1B spectrometer at the Laue-Langevin Institute in Grenoble, using neutrons of wavelength λ=2.5186 Å. The pattern of Mo₃Si₃ was measured in the 2θ interval 10.0 to 89.8° in steps of 0.2°. Mo₃Si₃ was housed in a 12 mm vanadium container. The structure was refined using the Hewat version of the Rietveld profile refinement programme. The values of the scattering length used for the two elements were as reported above. A list of observed and calculated intensities is available on request.

RESULTS AND DISCUSSIONS

Mo₃Si. The A15 structure, space group Pm₃n (No. 223), has the B-atoms placed in a body centered unit cell and the A-atoms in strings on the cubic faces of the unit cell. The direction of the strings are parallel to the axis of the unit cell and the interatomic distances between the metal atoms in the strings are approximately 10–15% smaller than the interatomic distances in the corresponding pure metal.¹¹ For the A15 compounds the parameters of the thermal ellipsoids of the A-atoms have lower values in the direction of the strings than perpendicular to this direction, so in general U₁₁ (Å) is smaller than U₃₃ (Å). For compounds that are superconductors, the ratio U₁₁/U₃₃ is smaller than the ratio a/4r where a is the unit cell parameter and r the Goldschmidt radius of the A-atom. For Nb₃Al and V₃Si the values are 0.645<0.887, and 0.792<0.881.

Table 1. Mo₃Si, Pm₃n, Mo in site 6c, Si in site 2a. Standard deviations in parentheses.

<table>
<thead>
<tr>
<th>h²+k²+l²&gt;</th>
<th>No. of reflections</th>
<th>R %</th>
<th>Scale factor</th>
<th>Isotropic ext. parameters</th>
<th>Mo-atom U₁₁, U₃₃ x10⁴</th>
<th>Si-atom U₁₁ x10⁴</th>
</tr>
</thead>
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<tr>
<td>1</td>
<td>128</td>
<td>2.1</td>
<td>54.6(5)</td>
<td>6.2(4)</td>
<td>15(1) 22(1)</td>
<td>27(1)</td>
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<tr>
<td>25</td>
<td>112</td>
<td>1.9</td>
<td>55.6(5)</td>
<td>7.2(4)</td>
<td>17(1) 24(1)</td>
<td>29(1)</td>
</tr>
<tr>
<td>50</td>
<td>92</td>
<td>1.9</td>
<td>57.3(7)</td>
<td>8.0(6)</td>
<td>20(1) 27(1)</td>
<td>34(2)</td>
</tr>
<tr>
<td>75</td>
<td>64</td>
<td>1.9</td>
<td>60.5(1.4)</td>
<td>8.6(9)</td>
<td>26(2) 32(2)</td>
<td>42(3)</td>
</tr>
<tr>
<td>85</td>
<td>56</td>
<td>1.9</td>
<td>64.1(1.8)</td>
<td>8.8(1.1)</td>
<td>32(3) 38(3)</td>
<td>50(3)</td>
</tr>
<tr>
<td>95</td>
<td>45</td>
<td>2.0</td>
<td>72.2(3.2)</td>
<td>11.2(1.6)</td>
<td>41(4) 47(4)</td>
<td>62(5)</td>
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<tr>
<td>100</td>
<td>41</td>
<td>1.9</td>
<td>72.9(3.3)</td>
<td>9.7(1.6)</td>
<td>43(4) 49(4)</td>
<td>64(5)</td>
</tr>
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Table 2. Atomic coordinates of Mo₃Si₃ from neutron diffraction powder pattern, R=10.1 %. Standard deviations in parentheses.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>B (Å²)</th>
</tr>
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<tr>
<td>Mo 1</td>
<td>16k</td>
<td>0.0786(6)</td>
<td>0.2247(6)</td>
<td>0</td>
<td>0.9(2)</td>
</tr>
<tr>
<td>Mo 2</td>
<td>4b</td>
<td>0</td>
<td>1/2</td>
<td>1/4</td>
<td>0.9(2)</td>
</tr>
<tr>
<td>Si 1</td>
<td>8h</td>
<td>0.1710(10)</td>
<td>0.6710(10)</td>
<td>0</td>
<td>0.9(2)</td>
</tr>
<tr>
<td>Si 2</td>
<td>4a</td>
<td>0</td>
<td>0</td>
<td>1/4</td>
<td>0.9(2)</td>
</tr>
</tbody>
</table>

respectively. For A15 compounds that show no superconductivity at moderately high temperatures, the values of the two ratios are close to each other. For Cr₃Si as an example, \( U_{11}/U_{33} \) is 0.879 and \( a/4r \) is 0.876. Mo₃Si belongs to this group of compounds and has \( a/4r \) equal to 0.875 and \( U_{11}/U_{33} \) equal to 0.878. Table 1 lists the results of the least-squares refinement of the Mo₃Si structure, including all the 128 observed reflections and selections of high angle data. The isotropic extinction parameter used assumes a Nelmes-Thornly formalism.

Refinement of the occupancy factor of the silicon atom showed that the composition did not deviate significantly from the stoichiometry of A₃B.

Mo₃Si₃. The compound was first reported to have the composition Mo₃Si₃, but later Aronsson showed Mo₃Si₃ to be isostructural with tetragonal W₅Si₅. According to this, the space group of Mo₃Si₃ is \( \text{i}4/mcm \) (No. 140) and the molybdenum atoms are placed in site 16k and 8b. The silicon atoms are placed in site 8h and 4a. The powder pattern of Mo₃Si₃ had fourteen resolved peaks and the profile refinement yielded the values of the parameters listed in Table 2. As starting parameters, the atomic coordinates for W₅Si₅ reported by Aronsson were used. The structure investigation of Mo₃Si₃ shows a good agreement between the atomic parameters of Mo₃Si₃ derived from a neutron diffraction powder pattern and the atomic parameters of W₅Si₅ obtained from a single crystal X-ray investigation.

The following Mo-Mo distances are found in Mo₃Si₃: 2.456(2) Å in a string of atoms parallel to the c-axis, 2.684(5) Å in the ab-plane, and 3.023(5) and 3.163(5) Å between atoms placed in planes spaced c/4 and c/2, respectively, from each other. In Mo₃Si the Mo-Mo distances are 2.449(1) and in molybdenum the interatomic distances are 2.725(1) Å. The Mo-Mo distances in Mo₃Si are thus 10 % shorter than in pure molybdenum.

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REFERENCES


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