Structure of Molten $Mn_{74}Si_{26}$ and Molten $Mn_{33.5}Si_{66.5}$ by Neutron Diffraction

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Molten $Mn_{74}Si_{26}$ and molten $Mn_{33.5}Si_{66.5}$ were investigated by neutron diffraction. The pair correlation function yielded, together with the X-ray results from a former paper, the partial coordination numbers, atomic distances, and the short range order parameter with the result that the atomic distribution in molten $Mn_{33.5}Si_{66.5}$ is statistical while the structure factor of molten $Mn_{74}Si_{26}$, as obtained with neutrons, shows a strong prepeak which means rather strong compound formation.

1. Introduction

In [1] we reported on X-ray diffraction experiments on molten $Mn_{74}Si_{26}$ and molten $Mn_{33.5}Si_{66.5}$. In the present paper we report on corresponding neutron diffraction experiments. Since the diameters of covalently bound Mn and Si, which amount to 2.34 Å and 2.22 Å, respectively [2], are rather different, and since the scattering length of Mn is negative [3], one can expect to obtain information concerning the chemical short range order parameter [4, 5] already with two scattering experiments instead of three which are usually necessary for the thorough investigation of a binary melt. For a description of the details of the experiment and the data reduction we refer to [6]. A summary of the notations used in this paper may be found in the review [7].

2. Experimental Fundamentals

2.1 *Specimen Preparation*

Manganese (99.999%) and silicone (99.99%) were melted together within an induction furnace and casted as rods with 6 mm diameter. Then the rods were grinded to fit into the crucibles.

2.2 *Crucibles*

Mn-Si melts are chemically highly aggressive. Therefore Al_2O_3-crucibles were used with cylindrical shape, an inner diameter of 6 mm, a wall thickness of 1 mm, and a height of 55 mm. Since manganese has a vapor pressure of about 1 Torr between 1100 °C and 1200 °C, the crucible was closed with a stopper made from sapphire. The crucibles consisted of an Al_2O_3-single crystal which yields only diffraction spots instead of rings. By suitable orientation of the crucible the appearance of diffraction peaks caused by the crucible can be avoided throughout the whole angle range. The adjustment of the empty crucible was made within the furnace. Then the specimen was brought into the crucible and the stopper was applied. The specimen was kept in molten state for about twenty hours. The subsequent chemical analysis showed no variation of the chemical composition.

2.3 *Furnace*

For the neutron diffractometer T2 at the Hahn-Meitner-Institute (Berlin, Germany) a furnace had to be built. This furnace works by direct current heating of a vanadium-tube (20 mm inner diameter; 0.1 mm wall thickness; 200 mm length) which surrounds the crucible. The height of the specimen to be irradiated by the neutron beam was 40 mm. The temperature of the melt during the neutron diffraction experiment was 1170 °C.

2.4 *Neutron Diffraction*

2.4.1 Molten $Mn_{74}Si_{26}$

The $Mn_{74}Si_{26}$-melt was investigated at the instrument T2 (Hahn-Meitner-Institut, Berlin), which is described in [8]. The wavelength was 2.399 Å. The multi-

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counter consisting of 400 single counters covered the Q-range $0.63\ \text{Å}^{-1} \leq Q \leq 3.52\ \text{Å}^{-1}$. The resolution was $\Delta 2\theta = 0.8°$, corresponding to $\Delta Q = 0.04\ \text{Å}^{-1}$ at $2\theta = 178°$.

2.4.2 Molten $Mn_{33.5}Si_{66.5}$

The $Mn_{33.5}Si_{66.5}$-melt was investigated at the instrument 7C2 (Lab. Léon Brillouin, Saclay), using the wavelength 0.704 Å. The multicounter consists of 640 single counters, and the Q-region was $0.8\ \text{Å}^{-1} \leq Q \leq 13.5\ \text{Å}^{-1}$. The measurement lasted for 20 hours, the temperature was 1170 °C.

3. Results and Discussion

3.1 Structure Factors

3.1.1 Molten $Mn_{74}Si_{26}$

In Fig. 1 we compare the total structure factor obtained with neutron diffraction from molten $Mn_{74}Si_{26}$ (solid line) and from amorphous $Mn_{74}Si_{23}P_3$ (broken line) [9]. The peak position at $2\ \text{Å}^{-1}$ is for the amorphous and the molten substance the same. From comparison with the X-ray structure factor in [1] one learns that the peak at $2\ \text{Å}^{-1}$ is a so-called prepeak, which means strong compound formation in the melt as well as in the amorphous state. A prepeak with amorphous $Mn_{74}Si_{23}P_3$ was also obtained by X-ray diffraction [9]. Table 1 shows the peak positions. The first peak at about $3\ \text{Å}^{-1}$ lies at lower values for the melt than for the amorphous state, i.e. the atomic distances are larger within the melt.

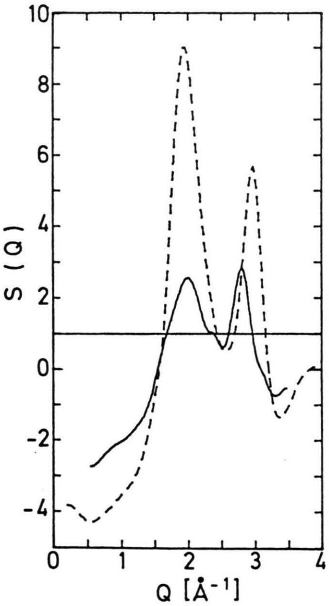

Fig. 1. Structure factor; neutron diffraction; (——) Molten $Mn_{74}Si_{26}$, (- - - -) Amorphous $Mn_{74}Si_{23}P_3$ [8].

3.1.2 Molten $Mn_{33.5}Si_{66.5}$

Figure 2 shows as broken line the structure factor from the X-ray experiment [1] and as solid line the structure factor as obtained from the neutron diffraction experiment according to [6] (back transformed curve).

3.2 Pair Correlation Functions

3.2.1 Molten $Mn_{74}Si_{26}$

For experimental reasons the structure factor of molten $Mn_{74}Si_{26}$ is only available up to $Q_{max} = 3.5\ \text{Å}^{-1}$, and therefore a Fourier-transformation makes no sense.

Table 1. Structure factor; neutron diffraction; molten $Mn_{74}Si_{25}$; amorphous $Mn_{74}Si_{23}P_3$; peak positions.

Substance	Prepeak Q [1/Å]	Main peak Q [1/Å]	*T* [°C]
$Mn_{74}Si_{26}$-melt	2.00	2.80	1170
$Mn_{74}Si_{23}P_3$ (amorphous)	1.94	2.97	–

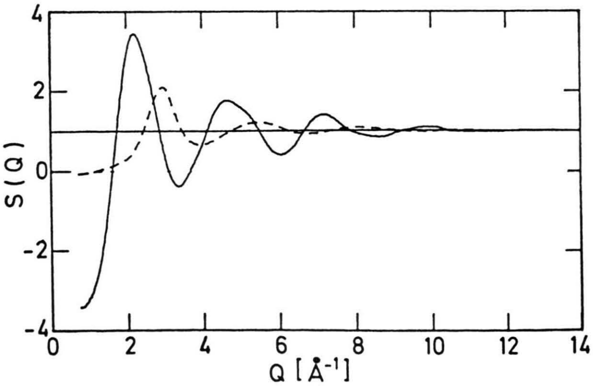

Fig. 2. Structure factor; molten $Mn_{33.5}Si_{66.5}$; 1170 °C; (——) Neutron diffraction, (- - - -) X-ray diffraction (Mo-Kα) [1].

3.2.2 Molten $Mn_{33.5}Si_{66.5}$

Figure 3 shows the total pair correlation function from the neutron diffraction experiment as solid line and from the X-ray diffraction experiment as broken line. In Table 2 the scattering lengths of the elements Mn, Si, and the alloy $Mn_{33.5}Si_{66.5}$ for X-rays as well as for neutrons are listed.

The total pair correlation functions $G_t^x(R)$ and $G_t^n(R)$ for X-rays and neutrons, respectively, depend on the partial correlation functions in the following way:

$$G_t^x(R) = 0.224\, G_{\mathrm{MnMn}}(R) + 0.277\, G_{\mathrm{SiSi}}(R) + 0.499\, G_{\mathrm{MnSi}}(R)\,, \tag{1}$$

$$G_t^n(R) = 0.622\, G_{\mathrm{MnMn}}(R) + 3.20\, G_{\mathrm{SiSi}}(R) - 2.82\, G_{\mathrm{MnSi}}(R)\,. \tag{2}$$

All weighting factors in the X-ray case are positive. The atomic diameters for covalent Mn and Si amount to $d_{\mathrm{Mn}}^{\mathrm{cov}} = 2.34$ Å and $d_{\mathrm{Si}}^{\mathrm{cov}} = 2.22$ Å, respectively [2]. The distance between covalent Mn and Si thus should be $R_{\mathrm{MnSi}}^{\mathrm{cov}} = 2.28$ Å. We further mention the atomic diameter of Mn, namely $d_{\mathrm{Mn}}^{\mathrm{at}} = 2.70$ Å [2].

i) Neutron Case

According to (2), the negative peak at 2.30 Å of the neutron curve of Figs. 3 and 4, respectively, can be due only to the shortest distance between Mn and Si, which was stated to be 2.28 Å for covalently bound Mn and Si.

The values of the diameter of covalently bound atoms as given above show that for R_{SiSi} a value of about 2.22 Å can be expected, which means that this distance lies also in the range of the negative peak of the neutron curve in Figs. 3 or 4. Thus we can estimate a coordination number Z' which contains the Si-Si – as well as the Mn-Si-pairs if we use as upper integration limit in (3) the crossing point R_0 of the solid line with the $G_t(R) = 0$-line:

$$Z' = \int_{R_{\mathrm{min}}^{\mathrm{l}}}^{R_0} (4\pi R^2 \varrho_0 + R\, G_t^{\mathrm{N}}(R))\, \mathrm{d}R = \frac{3.20}{c_{\mathrm{Si}}} Z_{\mathrm{SiSi}} - \frac{2.82}{c_{\mathrm{Si}}} Z_{\mathrm{MnSi}}\,. \tag{3}$$

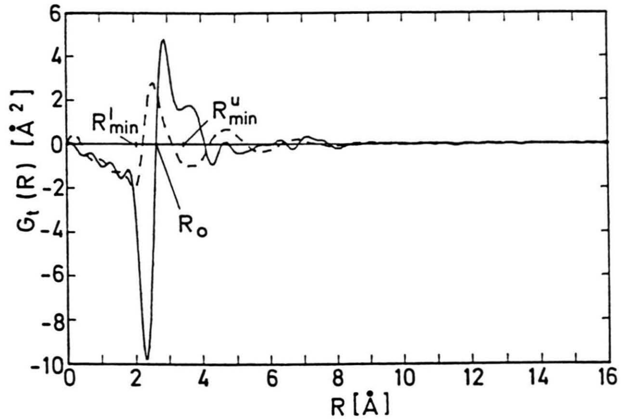

Fig. 3. Pair correlation function; molten $Mn_{33.5}Si_{66.5}$; (——) Neutron diffraction, (- - - -) X-ray diffraction (Mo-Kα) [1].

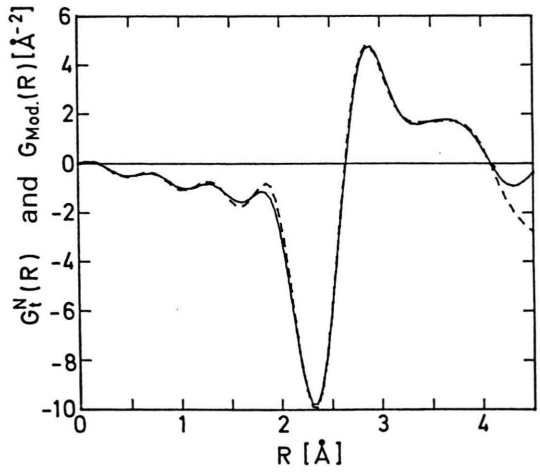

Fig. 4. Pair correlation function; molten $Mn_{33.5}Si_{66.5}$; (——) $G_t^{\mathrm{N}}(R)$, experimental curve, (- - - -) $G_{\mathrm{mod}}(R)$, modeled by fit of three Gaussians to $G_t^{\mathrm{N}}(R)$.

Table 2. Coherent scattering lengths of X-ray and neutrons for Mn, Si, and the alloy $Mn_{33.5}Si_{66.5}$.

	Mn	Si	$Mn_{33.5}Si_{66.5}$
X-rays [eu]	25	14	17.69
Neutrons [10^{-12} cm]	−0.373	0.426	0.158

The first positive peak of the neutron curve in Fig. 3 lies at 2.9 Å, which is in fair agreement not with the covalent diameter of Mn but with the atomic diameter of manganese $d_{\mathrm{Mn}} = 2.70$ Å [2]. Thus the positive contributions between R_0 and $R_{\mathrm{min}}^{\mathrm{u}}$ can be interpreted as Z_{MnMn} contributions:

$$Z'' = \int_{R_0}^{R_{\mathrm{min}}^{\mathrm{u}}} (4\pi R^2 \varrho_0 + R\, G_t^{\mathrm{N}}(R)\, \mathrm{d}R) = \frac{0.622}{c_{\mathrm{Mn}}} Z_{\mathrm{MnMn}}\,. \tag{4}$$

ii) X-Ray Case

The first peak of the X-ray curve in Fig. 3 starts at 2 Å, has its maximum value at 2.55 Å, and ends at about 3.6 Å. Looking also at the weighting factors in (1) it is reasonable to interpret the first peak of the X-ray curve as superposition of the peaks at $d_{\mathrm{SiSi}}^{\mathrm{cov}} = 2.22$ Å, $d_{\mathrm{MnSi}}^{\mathrm{cov}} = 2.28$ Å, and $d_{\mathrm{MnMn}}^{\mathrm{at}} = 2.70$ Å. Thus, the total coordination number Z''' is obtained as

$$Z''' = \int_{R_{\mathrm{min}}^{\mathrm{l}}}^{R_{\mathrm{min}}^{\mathrm{u}}} [4\pi R^2 \varrho_0 + R\, G_{\mathrm{t}}^{\mathrm{x}}(R)]\, \mathrm{d}R \qquad (5)$$

$$= \frac{0.224}{c_{\mathrm{Mn}}} Z_{\mathrm{MnMn}} + \frac{0.277}{c_{\mathrm{Si}}} Z_{\mathrm{SiSi}} + \frac{0.499}{c_{\mathrm{Si}}} Z_{\mathrm{MnSi}} \,.$$

The integration limits $R_{\mathrm{min}}^{\mathrm{l}}$ and $R_{\mathrm{min}}^{\mathrm{u}}$ are indicated in Figure 3. They correspond to the minima of the dashed line at the left-hand and right-hand side of the first peak.

This means under the presumptions mentioned, that from only two experiments all three partial coordination numbers may be obtained. The first column in Table 3 shows the partial coordination numbers as obtained from (3) to (5). Table 3 furthermore contains the Cargill-Spaepen short range order parameter $\eta = 0.07$ and the relative short range order parameter $\eta^0 = -0.09$, i.e. -9%. This means a weak segregation tendency.

3.2.3 Modeling of $G_{\mathrm{t}}^{\mathrm{N}}(R)$ for $Mn_{33.5}Si_{66.5}$

In a similar way as described in [10], a modeled total pair correlation function $G_{\mathrm{mod}}(R)$ was calculated by fitting three Gaussians to the experimental $G_{\mathrm{t}}^{\mathrm{N}}(R)$-curve. The first Gaussian was located at 2.30 Å, the second at 2.88 Å, and the third at 3.65 Å.

The solid line of Fig. 4 shows the experimental curve $G_{\mathrm{t}}^{\mathrm{N}}(R)$ up to $R = 4.5$ Å. The dashed line represents the result of the modeling procedure. From the Gaussians, the partial coordination numbers given in Table 4, second column, are obtained, which yield $\eta = +0.04$ and $\eta^0 = +7\%$. Thus the modeled curve yields as result a weak compound formation. Different attempts for Gaussian modeling yielded values in the region $-0.09 \leq \eta^0 \leq 0.07$. Therefore the distribution of Mn and Si in molten $Mn_{33.5}Si_{66.5}$ may be regarded as statistical. Molten $Ni_{81}P_{19}$ [10] and molten Au_xCs_{1-x} [11] showed a mixture of compound forming and segregation tendency. Therefore, looking at the phase diagram [12], also in molten $Mn_{33.5}Si_{66.5}$ coexistence of molten $Mn_{27}Si_{47}$ and Si could be possible. Since, however, the crystal structure of $Mn_{27}Si_{47}$ is not yet known, modeling was not possible.

Table 3. Atomic distances R_{ij}, partial coordination numbers Z_{ij}, Cargill-Spaepen chemical short range order (CSRO) parameter η, and Cargill-Spaepen relative CSRO-parameter η^0.

	From integration	From Gauss-fit
R_{MnSi}, R_{SiSi} [Å]	2.35	2.33
R_{MnMn} [Å]	2.90	2.91
Z_{MnMn}	7.0	4.6
Z_{SiSi}	4.9	5.6
Z_{MnSi}	7.2	7.8
Z_{SiMn}	3.6	3.9
η	−0.07	0.04
η^0	−0.09	0.07

Summary

Molten $Mn_{33.5}Si_{66.5}$ was investigated with neutron diffraction at about 50 °C above the melting temperature. The structure factor as well as the total pair correlation functions obtained from neutron and X-ray diffraction were compared. The atomic distances R_{MnSi}, R_{SiSi}, and R_{MnMn} were determined, as well as the partial coordination numbers Z_{MnSi}, Z_{SiMn}, Z_{SiSi}, and Z_{MnMn}. The Cargill-Spaepen short range order parameter indicates that molten $Mn_{33.5}Si_{66.5}$ shows statistical distribution. Neutron diffraction with molten $Mn_{74}Si_{26}$ and comparison with former X-ray diffraction work yielded a strong prepeak, which stands for compound formation within this melt.

[1] E. Nassif, P. Lamparter, B. Sedelmeyer, and S. Steeb, Z. Naturforsch. **38a,** 1093 (1983).

[2] Sargent-Welch, Scientific Corp., Periodic Table of the Elements, Catalogue Number S-18806, 1968, page 2

[3] L. Köster and W. B. Jelon, Neutron Diffraction Newsletter, 1983.

[4] B. E. Warren, X-Ray-Diffraction, Addison Wesley, Reading, Mass. 1969.

[5] G. S. Cargill and F. Spaepen, J. Non Cryst. Solids **43,** 91 (1981).

[6] B. Sedelmeyer, Doctor thesis, University of Stuttgart 1985.

[7] P. Lamparter and S. Steeb, pages 218–288 in "Materials and Science", Editors: Cahn, Haasen, Kramer, Verlag Chemie, Weinsberg 1993.

[8] G. A. Briggs and W. G. Sterling, Neutron Diffraction Facilities at Western European Medium Flux Reactors, ILL, Grenoble 1976.

[9] G. Rainer-Harbach, P. Lamparter, F. Paasche, and S. Steeb, Proc. 4th Int. Conf. on Rapidly Quenched Metals, Sendai 1989.

[10] B. Sedelmeyer and S. Steeb, Z. Naturforsch. **52a,** 284 (1997).

[11] W. Martin, W. Freyland, P. Lamparter, and S. Steeb, J. Phys. Chem. Liq. **10,** 77 (1980).

[12] G. Zwilling and H. Nowotny, Mh. Chemie **102,** 672 (1971).