

Neutron- and X-ray-Diffraction Study on the Structure of Amorphous $\text{Co}_{25}\text{Ti}_{75}$

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Amorphous $\text{Co}_{25}\text{Ti}_{75}$ could be produced using the melt-spin-technique. A neutron- and a X-ray-diffraction experiment was performed. Assuming $S_{\text{NC}} \equiv 0$ the partial Bhatia Thornton structure factors S_{NN} and S_{CC} as well as the partial coordination numbers were calculated. The discussion yields the atomic distances and the chemical short range order parameters.

Introduction

For the evaluation of the atomic structure of amorphous binary alloys one needs the three so-called partial structure factors. Therefore three diffraction experiments with chemically identical specimens must be performed. In the present case of amorphous $\text{Co}_{25}\text{Ti}_{75}$ in principle the method of neutron diffraction and isotopic substitution can be applied since there exist several convenient stable titanium isotopes such as Ti^{46} , for example. However, this isotope is only available as titanium dioxide. In spite of considerable efforts [1] up to now it was not possible to obtain amorphous melt-spun $\text{Co}_{25}^{\text{nat}}\text{Ti}_{75}^{46}$ -ribbons using metallic Ti^{46} obtained by chemical reduction. However, we succeeded in producing amorphous $\text{Co}_{25}^{\text{nat}}\text{Ti}_{75}^{\text{nat}}$. Thus, during the present work, we are restricted to one neutron- and one X-ray-diffraction experiment. Assuming the partial Bhatia-Thornton structure factor S_{NC} to be zero will lead to the two partial structure factors S_{NN} and S_{CC} . In a recent paper [1] it was shown that this is a rather rough approach and thus only yields a first approximation of the partial functions as well as of the chemical short range order parameter.

Concerning the equations and symbols as used in the present work we refer to [1] and [2].

Experimental

1. Specimen Preparation

Table 1 contains the scattering- and absorption-data of the elements used.

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The chemical purity of Co was 99.5%, that of Ti was 99%. The starting ingot was prepared by conventional electric arc melting in argon-atmosphere. Amorphous ribbons were produced using the melt spin technique within helium-atmosphere. The ribbon width amounted to 1 mm, the thickness was about 20 μm . For the specimens to be used with the neutron diffraction experiments the ribbons were put into vanadium cylinders (inner diameter 1.13 cm; wall thickness 0.1 mm). The final specimen height was 4.2 cm and was given by the distance between two boron nitride plugs which closed the vanadium tube. For the specimens to be used with the X-ray diffraction experiments the ribbons were cut in pieces 35 mm long and stuck on an aluminium frame with inner dimensions of 20 \times 30 mm^2 .

2. Apparatus

The neutron diffraction experiments were performed using the two axis diffractometer D4b at the high flux research reactor of the ILL (Grenoble). A description and the technical details of this instrument are given in [4]. The wavelength used was 0.704 Å. The scattered intensity was measured by two He^3 -detectors with 64 cells each.

Table 1. Scattering lengths b for coherent scattering and cross sections for incoherent scattering σ_{inc} and for absorption σ_{abs} for neutrons.

Element	σ_{inc} [barn]	b [10^{-12} cm]	σ_{abs} (0.704 Å) [barn]	Ref.
Co^{nat}	5.22	0.278	14.47	[3]
Ti^{nat}	2.71	−0.337	2.27	[3]

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The X-ray diffraction experiment was done using a diffractometer D 500 (Siemens, Karlsruhe). Always two runs were necessary with each specimen since the method of balanced filters was applied to extract the scattering signal corresponding to the Mo-K-radiation.

Results and Discussion

1. Total Structure Factors

a) Neutron Diffraction

Figure 1a shows the total Bhatia Thornton structure factor $S_n^{\text{BT}}(Q)$ of amorphous $\text{Co}_{25}\text{Ti}_{75}$ obtained by neutron diffraction. This function was derived from the measured data by correction for background scattering, scattering of the container and absorption within the specimen and the container according to [5]. The incoherent and the multiple

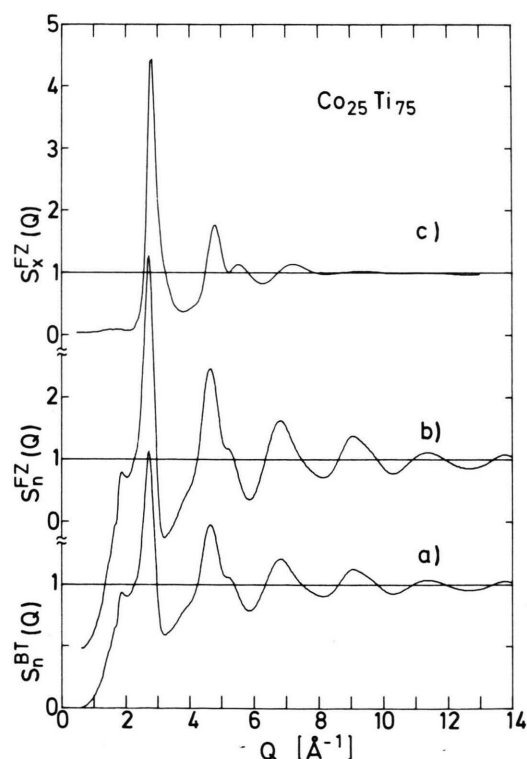


Fig. 1. a) Amorphous $\text{Co}_{25}\text{Ti}_{75}$; neutron diffraction; total Bhatia Thornton structure factor. b) Amorphous $\text{Co}_{25}\text{Ti}_{75}$; neutron diffraction; total Faber Ziman structure factor. c) Amorphous $\text{Co}_{25}\text{Ti}_{75}$; X-ray diffraction; total Faber Ziman structure factor.

scattering [6] were subtracted from the corrected intensity. The correction for inelastic scattering was done according to [7], the normalization according to [8]. The normalized coherently scattered intensity obtained yielded a preliminary Bhatia Thornton structure factor. Since this function for $Q=0$ amounted 0.29 which is much larger than is to be expected due to the isothermal compressibility, and since this function did not oscillate properly around the horizontal line at 1 we concluded that an additional correction term had to be subtracted in order to yield the final $S_n^{\text{BT}}(Q)$. As this additional term was not known theoretically it was assumed to be a Gaussian function $u(Q)$ which is shown in Fig. 2 as broken line. The subtraction of this function from the preliminary structure factor yielded the Bhatia Thornton structure factor shown in Fig. 1a which fulfilled the following two criteria presumed that $u(Q)$ was chosen properly:

- i) It approaches zero for $Q = 0$.
- ii) At the Q positions which are the arithmetic mean of succeeding maxima- and minima-positions of $S_n^{\text{BT}}(Q)$ the mean values of the corresponding maxima and minima are close to 1.

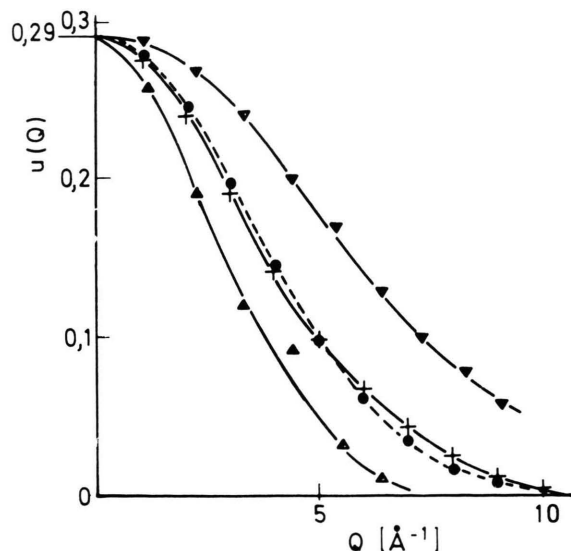


Fig. 2. Background curves $u(Q)$ (see text) normalized to 0.29 at $Q=0$. (●●●) Background curve used for the present correction; (▼▼▼) hydrogen scattering; (+++) magnetic scattering of Co^{3+} ; (▲▲▲) magnetic scattering of Ti^{3+} .

To reveal the physical origin of this background, Fig. 2 shows also the normalized contribution of hydrogen incoherent scattering [9, 10] and of magnetic scattering from Co³⁺ [11] and Ti³⁺ [10]. Apparently, the magnetic scattering of Co³⁺ is the most likely source of this scattering contribution $u(Q)$.

Figure 1b shows the Faber Ziman total structure factor calculated from the total Bhatia Thornton structure factor of Figure 1a.

b) X-ray Diffraction

The measured X-ray intensity obtained with amorphous Co₂₅Ti₇₅ was corrected for polarization and absorption [12] and normalized according to [8]. The atomic scattering lengths were taken from [13] and corrected for anomalous dispersion according to [14]. After subtraction of the Compton intensity [12] the total Faber Ziman structure factor $S_x^{FZ}(Q)$ as shown in Fig. 1c was obtained.

c) Discussion of the Total Structure Factors

The neutron Faber Ziman total structure factor $S_n^{FZ}(Q)$ from Fig. 1b becomes negative in the region $Q < 1.7 \text{ \AA}^{-1}$. This is caused by the fact that during the calculation of $S_n^{FZ}(Q)$ from the coherently scattered intensity the so called monotonic Laue scattering $c_{\text{Co}}c_{\text{Ti}}(b_{\text{Co}} - b_{\text{Ti}})^2$ has to be subtracted. This negative run indicates nonstatistical distribution of the atoms of different kinds around each other.

Furthermore $S_n^{FZ}(Q)$ exhibits a pronounced prepeak at $Q = 1.9 \text{ \AA}^{-1}$. This again indicates a tendency to compound formation in amorphous Co₂₅Ti₇₅.

2. Partial Bhatia Thornton Structure Factors

Under the assumption $S_{\text{NC}}(Q) = 0$ from the total $S_n^{\text{BT}}(Q)$ and $S_x^{\text{BT}}(Q)$ the partial structure factors $S_{\text{NN}}(Q)$ and $S_{\text{CC}}(Q)$ were calculated and shown in Figure 3. $S_{\text{CC}}(Q)$ shows pronounced oscillations which give evidence for a chemical ordering effect. Also attention should be paid to the fact that the prepeak in Fig. 1a mainly appears in $S_{\text{CC}}(Q)$. For the present case of amorphous Co₂₅Ti₇₅, the X-ray and neutron total functions, respectively, are related

to the partials by

$$S_x^{\text{BT}}(Q) = 0.991 S_{\text{NN}}(Q) + 0.009 S_{\text{CC}}(Q), \quad (1)$$

$$S_n^{\text{BT}}(Q) = 0.321 S_{\text{NN}}(Q) + 0.679 S_{\text{CC}}(Q). \quad (2)$$

Apparently the X-ray curve is given mainly by $S_{\text{NN}}(Q)$, i.e. the topological arrangement of the atoms, whereas the neutron curve rather reflects $S_{\text{CC}}(Q)$, i.e. the chemical ordering.

3. Total Pair Correlation Functions

The Faber Ziman total structure factors in Figs. 1b and 1c yield the total pair correlation functions $G^{FZ}(Q)$ shown in Figs. 4a and 4b. For the present case of amorphous Co₂₅Ti₇₅ the relationships between the X-ray- and neutron-FZ total pair correlation functions, respectively, and the partial pair correlation functions are

$$G_x^{FZ}(R) = 0.084 G_{\text{CoCo}}(R) + 0.504 G_{\text{TiTi}}(R) + 0.412 G_{\text{CoTi}}(R), \quad (3)$$

$$G_n^{FZ}(R) = 0.144 G_{\text{CoCo}}(R) + 1.902 G_{\text{TiTi}}(R) - 1.046 G_{\text{CoTi}}(R). \quad (4)$$

We learn from (3) that G_{CoCo} does merely influence $G_x^{FZ}(R)$ in Figure 4b. The pronounced minimum in $G_n^{FZ}(R)$ of Fig. 4a according to (4) can only be caused by $G_{\text{CoTi}}(R)$ whereas the maximum must be ascribed to $G_{\text{TiTi}}(R)$. The resulting distances 2.37 Å for Co–Ti and 2.93 Å for Ti–Ti are not reliable since the minimum and the maximum overlap,

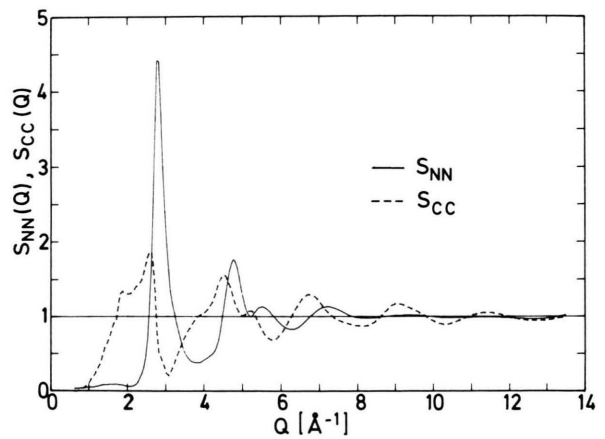


Fig. 3. Amorphous Co₂₅Ti₇₅; partial Bhatia Thornton structure factors.

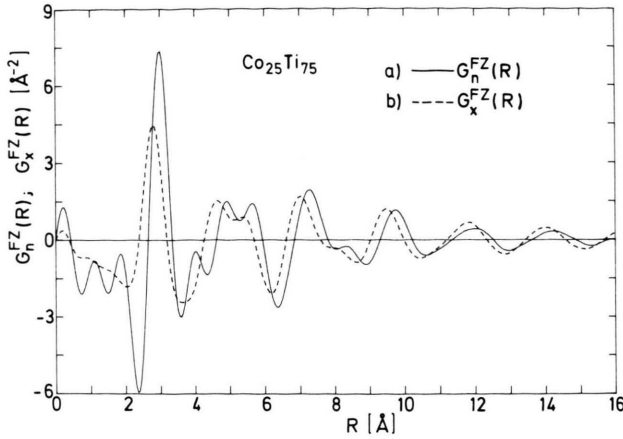


Fig. 4. a) Amorphous $\text{Co}_{25}\text{Ti}_{75}$; neutron diffraction; total Faber Ziman pair correlation function. b) Amorphous $\text{Co}_{25}\text{Ti}_{75}$; X-ray diffraction; total Faber Ziman pair correlation function.

which causes a nonsymmetric shape of both extrema. Therefore another method was used to extract atomic distances [15], which will be described in the following.

4. Atomic Distances

To determine the distances between different atomic species from the neutron pair correlation function $G_n^{\text{FZ}}(R)$, part of the X-ray pair correlation function $G_x^{\text{FZ}}(R)$ was subtracted or added in such a way that one of the partials $G_{ij}(R)$ vanishes in each case. Then the resulting curves were multiplied in such a way that the sum of the weighting factors of the two remaining partial pair correlation functions yields one. Thus the functions $G1(R)$, $G2(R)$, and $G3(R)$ were obtained according to (5), (6) and (7) and presented in Figure 7.

$$G1(R) = -1.457 G_{\text{TiTi}}(R) + 2.457 G_{\text{CoTi}}(R), \quad (5)$$

$$G2(R) = 0.063 G_{\text{CoCo}}(R) + 0.937 G_{\text{CoTi}}(R), \quad (6)$$

$$G3(R) = 0.101 G_{\text{CoCo}}(R) + 0.899 G_{\text{TiTi}}(R). \quad (7)$$

We recognize that $G2(R)$ is convenient to determine the distance Co–Ti and $G3(R)$ correspondingly for the distance Ti–Ti since the weighting-factor of $G_{\text{CoCo}}(R)$ in both cases is small. The diameter of the Co-atoms d_{CoCo} follows from

$$d_{\text{CoCo}} = 2d_{\text{CoTi}} - d_{\text{TiTi}}. \quad (8)$$

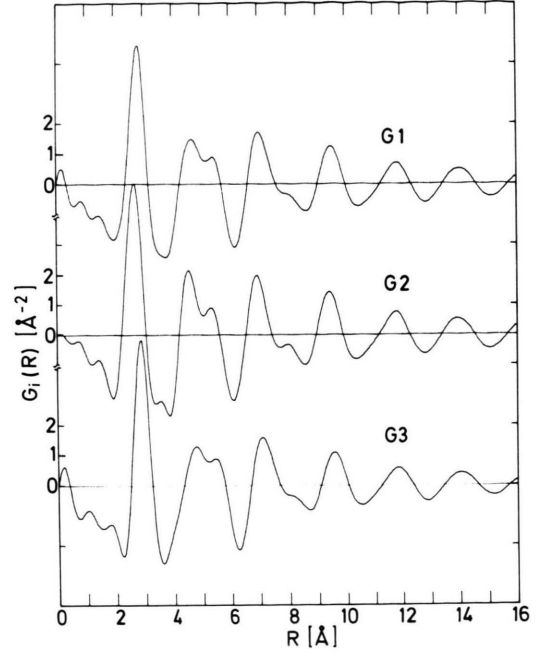


Fig. 5. Amorphous $\text{Co}_{25}\text{Ti}_{75}$; difference curves from $G_x(R)$ and $G_n(R)$ (see text).

Table 2. Amorphous $\text{Co}_{25}\text{Ti}_{75}$; atomic distances; * calculated according to (8).

	d_{exp} [Å]	d_G [Å]	$\frac{1}{2} (d_G^{\text{Co}} + d_G^{\text{Ti}})$
Co–Co	2.52*	2.50	—
Ti–Ti	2.89	2.91	—
Co–Ti	2.70	—	2.71

The distances obtained in such a way are given in Table 2, which contains also the Goldschmidt-diameters d_G [16].

The agreement between the experimental distances and the Goldschmidt diameters is good.

5. Partial Pair Correlation Functions

From the partial structure factors $S_{\text{NN}}(Q)$ and $S_{\text{CC}}(Q)$ in Fig. 3 the partial pair correlation functions $G_{\text{NN}}(R)$ and $G_{\text{CC}}(R)$ were calculated and presented in Figure 6.

a) Partial Coordination Numbers

By integration along the main peak of the two Faber Ziman total pair correlation functions $G_n^{\text{FZ}}(R)$

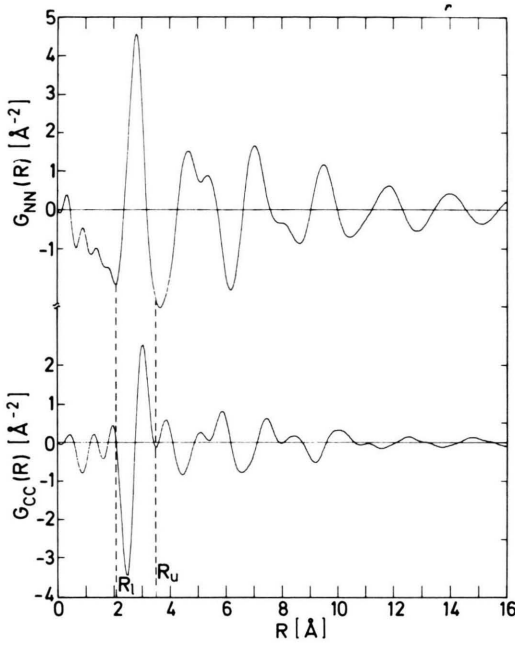


Fig. 6. Amorphous $\text{Co}_{25}\text{Ti}_{75}$; partial Bhatia Thornton pair correlation functions.

and $G_x^{\text{FZ}}(R)$ from Fig. 4a and 4b one obtains according to (9) two total coordination numbers Z_k :

$$Z_k = \int_{R_{l_k}}^{R_{u_k}} [4\pi R^2 \varrho_0 + R \cdot G_k(R)] dR \quad (9)$$

with $k = n$ (neutrons) or x (X-rays), ϱ_0 = mean atomic number density = 0.072 Å^{-3} .

Z_k can be presented in terms of the partial coordination numbers Z_{ij} , which yields two equations for the Z_{ij} according to (10):

$$Z_k = \frac{W_{\text{CoCo}}}{C_{\text{Co}}} Z_{\text{CoCo}} + \frac{W_{\text{TiTi}}}{C_{\text{Ti}}} Z_{\text{TiTi}} + \frac{W_{\text{CoTi}}}{C_{\text{Ti}}} Z_{\text{CoTi}}. \quad (10)$$

Z_{ij} means the number of j -atoms around an i -atom. The 3rd equation for the Z_{ij} can be deduced from the assumption $S_{\text{NC}} = 0$ as shown in [1], and one obtains

$$Z_{\text{CoCo}} - Z_{\text{TiTi}} + \left(1 - \frac{C_{\text{Co}}}{C_{\text{Ti}}}\right) Z_{\text{CoTi}} = 0. \quad (11)$$

Thus the system of three equations for the determination of the partial coordination numbers is as follows:

$$Z_x = 0.336 Z_{\text{CoCo}} + 0.672 Z_{\text{TiTi}} + 0.549 Z_{\text{CoTi}}, \quad (12)$$

$$Z_n = 0.576 Z_{\text{CoCo}} + 2.536 Z_{\text{TiTi}} - 1.395 Z_{\text{CoTi}}, \quad (13)$$

$$0 = 0.188 Z_{\text{CoCo}} - 0.188 Z_{\text{TiTi}} + 0.125 Z_{\text{CoTi}}. \quad (14)$$

Taking R_u and R_l in (9) according to the so-called minimum-minimum-method, the total correlation functions yielded $Z_x = 14.2$ and $Z_n = 13.4$. Table 3 contains the partial coordination numbers.

$i-j$	Z_{ij}	Table 3. Amorphous $\text{Co}_{25}\text{Ti}_{75}$; partial coordination numbers Z_{ij} .
Co-Co	3.2	
Ti-Ti	10.6	
Co-Ti	11	
Ti-Co	3.7	

b) Short Range Order Parameters [17], [18]

Using the partial coordination numbers from Table 3 the total number of atoms around a cobalt atom amounts to $Z_{\text{Co}} = 14.2$ and around a titanium atom to $Z_{\text{Ti}} = 14.3$. The normalized Cargill Spaepen short range order parameter amounts to 9%. This means a preference of compound formation. The normalized Warren Cowley short range order parameter α can be determined from the Bhatia Thornton partial functions by using the equations

$$\alpha = \int_{R_l}^{R_u} R \cdot G_{\text{CC}}(R) dR / Z_{\text{NN}}, \quad (15)$$

$$Z_{\text{NN}} = \int_{R_l}^{R_u} [4\pi R^2 \varrho_0 + R \cdot G_{\text{NN}}(R)] dR. \quad (16)$$

With $R_l = 2.09 \text{ Å}$ and $R_u = 3.53 \text{ Å}$ (see Fig. 6) we obtain $\alpha = -0.037$, which yields finally as normalized Warren Cowley short range order parameter $\alpha^\circ = -11\%$. This again shows the dominance of compound formation within amorphous $\text{Co}_{25}\text{Ti}_{75}$.

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