

Neutron- and X-Ray-Diffraction Study on the Structure of Amorphous Cu₅₀Ti₅₀

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Using the method of isotopic substitution from two neutron- and one X-ray-diffraction experiment the three partial Bhatia Thornton- as well as Faber Ziman-structure factors were determined with amorphous Cu₅₀Ti₅₀. The discussion yields the partial coordination numbers and atomic distances as well as the short range order parameters.

Experimental

For the evaluation of the atomic structure of amorphous binary alloys one needs the three partial structure factors. Therefore three diffraction experiments must be performed with chemically identical specimens but with appropriate variations of the scattering factors of the constituents. In the present case of amorphous Cu₅₀Ti₅₀ two neutron- and one X-ray diffraction experiments should yield the most reliable results. Besides copper of natural isotopic abundance two isotopic mixtures containing mainly Cu⁶³ and Cu⁶⁵, respectively, were available. The present results will be discussed together with the results of diffraction experiments as reported in the literature [1–4]. In those papers with amorphous Cu_xTi_{1-x}-alloys (0.50 ≤ x ≤ 0.66) the total Faber Ziman structure factor and the two Bhatia Thornton partial structure factors *S*_{NN} and *S*_{CC}, respectively, were evaluated, the latter ones by assuming *S*_{NC} to be zero.

As for the reduction of the experimental data and the symbols and the theoretical relations used in the present work we refer to [5, 6].

Table 1 contains the scattering – and absorption – data of the elements and isotopic mixtures used

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during the present study:

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

Element	<i>σ</i> _{inc} [barn]	<i>b</i> [10 ⁻¹² cm]	<i>σ</i> _{abs} (0.704 Å) [barn]	Reference
Ti ^{nat}	2.71	−0.337	2.27	[7]
Cu ^{nat}	0.50	0.7689	1.53	[7]
*Cu ⁶³	0.013	0.659	1.808	[8]
*Cu ⁶⁵	0.39	1.014	0.915	[8]

The *Cu⁶³-mixture was enriched with 98.2% of Cu⁶³, whereas the *Cu⁶⁵-mixture contained 96.7% Cu⁶⁵. The chemical purity of Ti^{nat} was 99%, that of Cu^{nat} was 99.9%. In an induction furnace under argon-atmosphere the three alloys Cu^{nat}₅₀Ti₅₀, *Cu⁶³₅₀Ti₅₀, and *Cu⁶⁵₅₀Ti₅₀ were melted and then cast into a molybdenum ingot mold to obtain cylindrical specimens with 6 mm diameter. 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 cut in pieces 5 mm long, put into vanadium cylinders (inner diameter 1.13 cm; wall thickness 0.1 mm) which were closed by boron nitride plugs. The final specimen height was 4.2 cm, which was given by the distance of the boron nitride plugs.

The neutron diffraction experiments were performed using the two axis diffractometer 7C2 at the research reactor Orphée of the Laboratoire Léon

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Brillouin at Saclay (France). A description and the technical details of this instrument are given in [9]. The wavelength used was 0.704 Å. The detector was a BF₃-multidetector consisting of 640 cells in a mutual distance of 0.2°.

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 aluminum frame with inner dimensions of 20 × 30 mm².

The X-ray diffraction experiment was done using a diffractometer D5000 (Siemens, Karlsruhe). Always two runs were necessary with each specimen since the method of balanced filters was applied to extract the diffracted intensity corresponding to the Mo-K_α-wavelength.

Results and Discussion

1. Total Structure Factors

Figure 1 shows the total Bhatia Thornton structure factors as obtained using neutron- and X-ray-diffraction with amorphous Cu₅₀Ti₅₀. The corresponding total Faber Ziman structure factors $S^{FZ}(Q)$ are not shown here. The neutron diffraction curves show a pronounced prepeak at $Q = 2 \text{ Å}^{-1}$. The intensity of this prepeak depends on the weighting factor W_{CC} of S_{CC} :

$$W_{CC} = c_{Cu} c_{Ti} (b_{Cu} - b_{Ti})^2 (c_{Cu} b_{Cu}^2 + c_{Ti} b_{Ti}^2)^{-1} \quad (1)$$

with c_{Cu} , c_{Ti} = atomic fractions ($c_{Cu} + c_{Ti} = 1$).

Furthermore it depends on the degree of chemical short range order (CSRO). Since the neutron-scattering lengths of both components differ in their signs, the weighting factor becomes rather large (compare Table 2). Thus already a small oscillation of S_{CC} itself may give rise to a rather large prepeak. The same stands for the cross correlation function $S_{NC}(Q)$ which arises from the difference of the atomic volumina of both components.

2. Partial Structure Factors

Figure 2 shows the partial Bhatia Thornton structure factors calculated from the three totals shown in Figure 1. It may be noted that according to Table 2 four equations for the evaluation of the three partials were at our disposal. However, the neutron experiment with the Cu^{nat}-sample did show rather small contrast to the two isotopic-enriched samples. Therefore it turned out that the neutron

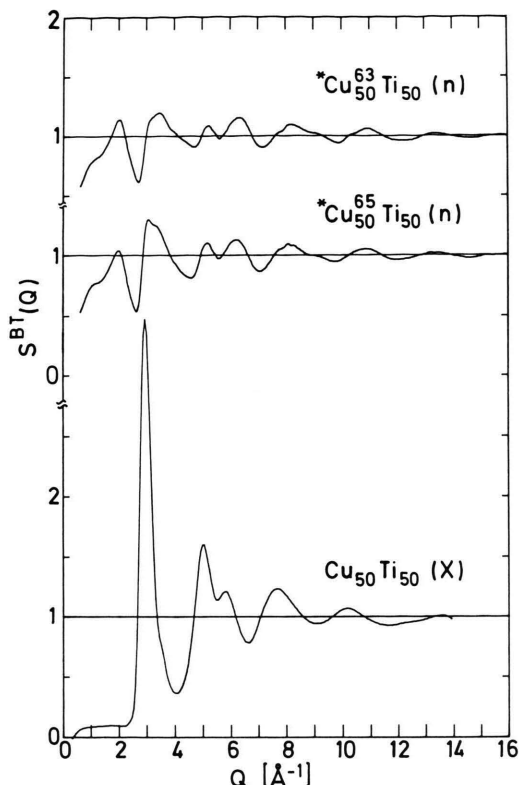


Fig. 1. Amorphous Cu₅₀Ti₅₀: Total Bhatia Thornton structure factors $S^{BT}(Q)$; neutron (n)- and X-ray (X)-diffraction.

Table 2. Weighting factors of the partial Faber Ziman structure factors a_{ij} and the partial Bhatia Thornton structure factors S_{ij} .

Radiation	Specimen	a_{CuCu}	a_{TiTi}	a_{CuTi}
n	Cu ^{nat} ₅₀ Ti ₅₀	3.169	0.609	-2.778
n	*Cu ⁶³ ₅₀ Ti ₅₀	4.189	1.095	-4.284
n	*Cu ⁶⁵ ₅₀ Ti ₅₀	2.243	0.248	-1.491
X	Cu ^{nat} ₅₀ Ti ₅₀	0.32	0.19	0.49
Radiation	Specimen	S_{NN}	S_{CC}	S_{NC}
n	Cu ^{nat} ₅₀ Ti ₅₀	0.132	0.868	1.355
n	*Cu ⁶³ ₅₀ Ti ₅₀	0.095	0.905	1.171
n	*Cu ⁶⁵ ₅₀ Ti ₅₀	0.201	0.799	1.602
X	Cu ^{nat} ₅₀ Ti ₅₀	0.98	0.02	0.54

curves of the latter two samples combined with an X-ray curve yielded the most reliable results. The partial function $S_{NN}(Q)$ shows pronounced maxima and minima, whereas $S_{CC}(Q)$ is surprisingly monotonic but nevertheless indicates by the prepeak at $Q = 2 \text{ Å}^{-1}$ chemical short range order. Also S_{NC} is

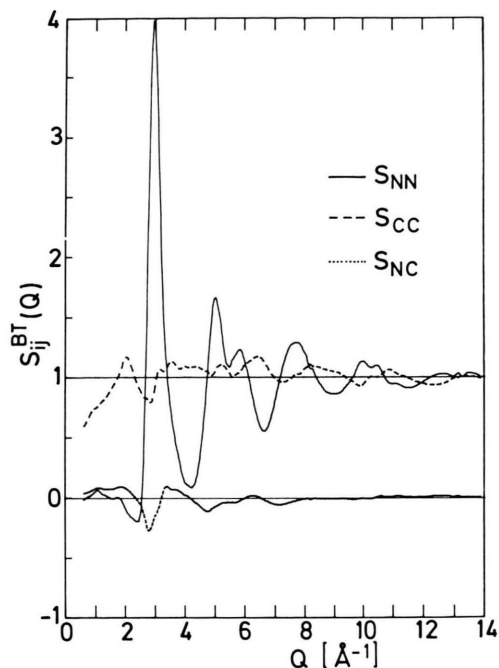


Fig. 2. Amorphous $\text{Cu}_{50}\text{Ti}_{50}$: Partial Bhatia Thornton structure factors.

compared to S_{NN} rather monotonic but nevertheless shows a small size effect.

In the following we will discuss, whether the partial structure factor $S_{NC}(Q)$ can be neglected as was done in [4]. For this purpose $\tilde{S}_{NN}(Q)$ as well as $\tilde{S}_{CC}(Q)$ were calculated assuming $S_{NC}(Q) \equiv 0$ from the total $S(Q)$ -functions obtained using X-rays and neutrons, respectively, with a $\text{Cu}_{50}\text{Ti}_{50}$ -specimen made from copper with natural isotopic abundance. These functions were compared in Fig. 3 as well as Fig. 4 with the partial functions $S_{NN}(Q)$ and $S_{CC}(Q)$ from Figure 2. While $S_{NN}(Q)$ shows only minor variations caused by neglecting $S_{NC}(Q)$, the change in $S_{CC}(Q)$ is considerable. Obviously the assumption $S_{NC}(Q) = 0$ results in an enhancement of the oscillations of $\tilde{S}_{CC}(Q)$ compared to those of $S_{CC}(Q)$. This effect, already noted for the case $\text{Ti}_{84}\text{Si}_{16}$ in [10], apparently is a general one for metallic glasses exhibiting a size effect.

Figure 5 shows the Faber Ziman partial structure factors. The prepeak already mentioned before appears only in $S_{\text{CuCu}}(Q)$ but not in $S_{\text{TiTi}}(Q)$, which behaviour reflects the asymmetry of the short range order with respect to the two constituents. It can be explained as follows: In contrast to statistical dis-

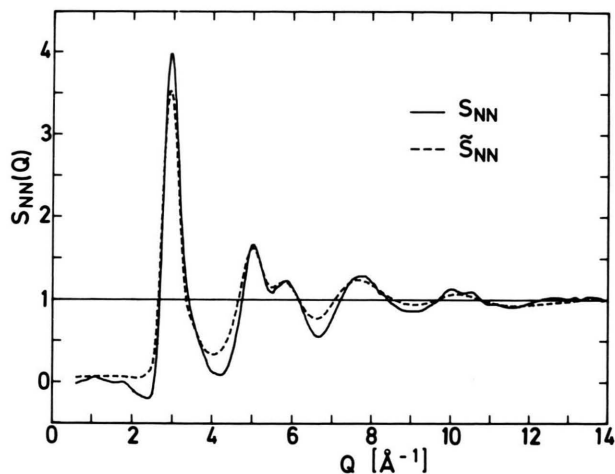


Fig. 3. Amorphous $\text{Cu}_{50}\text{Ti}_{50}$: Partial Bhatia Thornton structure factors $S_{NN}(Q)$ and $\tilde{S}_{NN}(Q)$. $\tilde{S}_{NN}(Q)$ results with the assumption $S_{NC} = 0$.

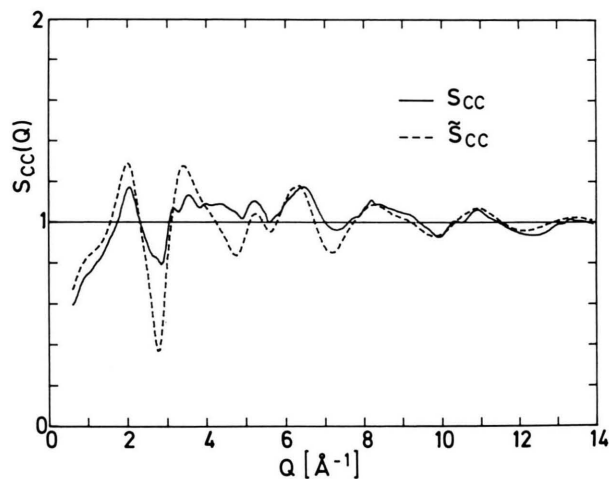


Fig. 4. Amorphous $\text{Cu}_{50}\text{Ti}_{50}$: Partial Bhatia Thornton structure factors $S_{CC}(Q)$ and $\tilde{S}_{CC}(Q)$. $\tilde{S}_{CC}(Q)$ results with the assumption $S_{NC} = 0$.

tribution of both atomic species a Cu–Cu distance larger than the nearest neighbour distance is favoured in the Cu–Ti glass which gives rise to a prepeak at a smaller Q -value than that of the main peak in $S_{\text{CuCu}}(Q)$. Thus it may be interpreted as arising from a well defined Cu–Cu-distance which occurs often and is fixed by a titanium atom bound between two Cu-atoms by means of a certain compound forming tendency. The main peak in S_{CuCu} is rather asymmetric.

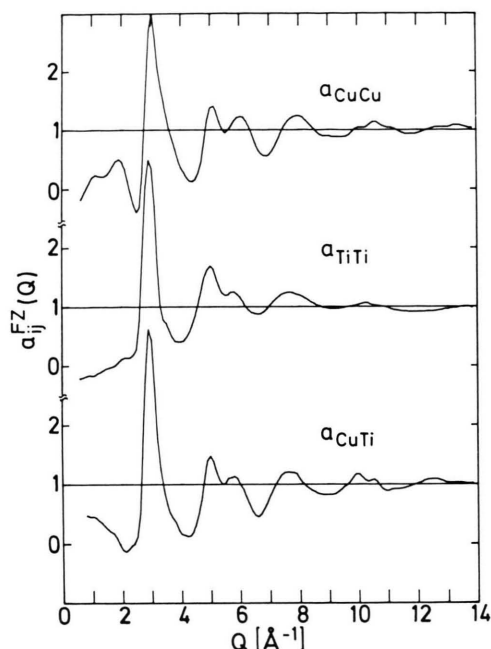


Fig. 5. Amorphous $\text{Cu}_{50}\text{Ti}_{50}$: Partial Faber Ziman structure factors.

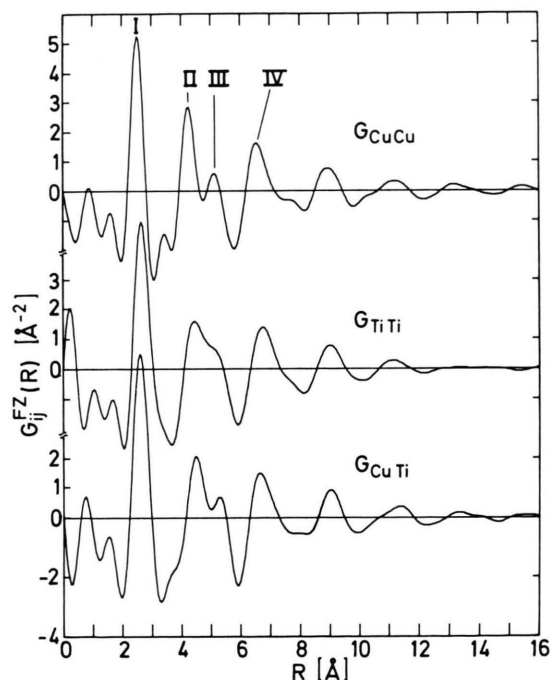


Fig. 6. Amorphous $\text{Cu}_{50}\text{Ti}_{50}$: Partial Faber Ziman pair correlation functions.

3. Pair Correlation Functions

Figure 6 shows the partial pair correlation functions as obtained from the partial Faber Ziman structure factors of Fig. 5 by Fourier transformation. The coordination shell III in $G_{\text{TiTi}}(R)$ appears only as a shoulder on shell II, whereas in $G_{\text{CuCu}}(R)$ as well as in $G_{\text{CuTi}}(R)$ shell II and shell III are well separated. This means that the distances between a Cu-atom at $R = 0$ and any other atom in shell II or shell III are well defined, whereas for a Ti-atom at $R = 0$ the positions of the other Ti-atoms in shell II and shell III are smeared out.

The main maxima in Fig. 6 show almost the same positions which means that the atoms of both components in this glass have nearly the same diameters.

The distances tabulated in Table 3 were obtained from Figure 7.

Atomic pair ij	R_{ij} [Å]
Cu–Cu	2.50
Ti–Ti	2.65
Cu–Ti	2.60

Table 3. Amorphous $\text{Cu}_{50}\text{Ti}_{50}$: Nearest neighbour distances.

Table 4 shows the atomic radii for Cu and Ti as well as those for covalent binding.

Element	Cu	Ti
covalent radii [Å]	1.17	1.32
atomic radii [Å]	1.28	1.47

Table 4. Atomic and covalent radii.

The Ti–Ti distance obtained in Table 3 is surprisingly short and agrees well with the diameter of covalent bound Ti from Table 4, whereas the Cu–Cu distance points rather on the diameter of atomic Cu. Also it is remarkable that the Cu–Ti distance of 2.60 Å from Table 3 corresponds exactly to the sum of the covalent bound Ti-radius and the atomic Cu-radius from Table 4.

From the partial $G_{ij}(R)$ -functions the partial coordination numbers Z_{ij} are calculated by integration:

$$Z_{ij} = c_j \int_{R_1}^{R_0} \{4\pi R^2 \cdot \varrho_0 + R \cdot G_{ij}(R)\} dR \quad (2)$$

with ϱ_0 = mean atomic number density = 0.068 Å^{-3} .

Table 5. Amorphous C₅₀Ti₅₀: Partial coordination numbers.

Atomic pair <i>i-j</i>	Minimum-minimum		Symmetrization	
	<i>R</i> _l [Å]; <i>R</i> _u [Å]	<i>Z</i> _{<i>ij</i>}	<i>R</i> _l [Å]; <i>R</i> _u [Å]	<i>Z</i> _{<i>ij</i>}
Cu–Cu	2.00; 3.07	4.51	2.00; 3.04	4.53
Ti–Ti	2.07; 3.67	6.39	2.07; 3.21	5.74
Cu–Ti	2.00; 3.33	5.96	2.00; 3.24	5.96

The upper and lower integration limits *R*_u and *R*_l depend on the method of evaluation. In the present paper the so-called minimum-minimum-method and the so-called symmetrization-method were applied. Table 5 shows the corresponding partial coordination numbers. Since the atomic concentrations of both components are equal it stands

$$Z_{\text{CuTi}} = Z_{\text{TiCu}} \quad (3)$$

4. Sort Range Order Parameters [11], [12]

Using the partial coordination numbers from Table 5 the total number of atoms around a copper atom amounts to *Z*_{Cu} = 10.47 and around a titanium atom to *Z*_{Ti} = 12.35. The normalized Cargill Spaepen short range order parameter [11] according to the minimum-minimum method amounts of 6.1% and that obtained according to the symmetrization method to 8.6%. This means a preference of compound formation.

The normalized Warren Cowley short range order parameter [12] was also calculated from the partial coordination numbers [6]. Independently of the minimum-minimum-or the symmetrization method for the determination of the coordination numbers – 14% was obtained. This also means a slight tendency to compound formation.

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