Determination of Partial Structure Factors of Molten Eutectic $Ni_{33}Ge_{67}$

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Using isotopic substitution and X-ray scattering, different weighted structure factors were measured and combined in order to calculate partial structure factors. Although we got an overdetermined system of equations, the solution of this problem was difficult due to the small value of the determinant. From the partial pair correlation functions and the radial concentration correlation function a splitting of the first coordination shell is obvious. The dip in S_{Ni-Ge} and the corresponding peak in S_{Ni-Ni} indicate some degree of charge transfer in the melt.

Introduction

Eutectic concentrations are very interesting points in phase diagrams. During the phase transition liquid-solid two processes seem to occur simultaneously: the segregation into the eutectic components and their solidification.

For a better understanding of this process, detailed knowledge about the short-range order in the melt is needed.

In this way we combined neutron diffraction experiments on molten eutectic $Ni_{33}Ge_{67}$, using isotopic substitution, and an X-ray experiment in order to extract partial structure factors. The phase diagram of Ni–Ge [1] shows several phases and phase transitions below the liquidus line. Besides the eutectic $Ni_{33}Ge_{67}$ two additional eutectic points are present at the Ni rich side of the phase diagram.

Structural investigations, done by X-ray, reported segregation of Ge rich melts into Ge-clusters and clusters having a structure like Ni_5Ge_3 [2] or $NiGe_2$ [3] (but $NiGe_2$ does not exist in the phase diagram given in [1]).

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Experimental

The X-ray diffraction experiment on molten $Ni_{33}Ge_{67}$ and pure molten Ge were carried out on a $\Theta-\Theta$-diffractometer described in [4]. The measured intensity was corrected for polarization and Compton scattering and, after normalization, the structure factor in the Faber-Ziman form [5] was calculated.

The neutron scattering experiments, using samples with natural nickel *Ni (scattering length $b = 1.03 \cdot 10^{-14}$ cm), a mixture of ^{60}Ni and *Ni ($b = 0.5 \cdot 10^{-14}$ cm) and ^{58}Ni ($b = 1.44 \cdot 10^{-14}$ cm), were done at the diffractometer 7C2 of the laboratory "Léon Brillouin" (Saclay).

A third experiment with ^{62}Ni, ^{60}Ni and *Ni mixed in such a way that $b_{Ni} = 0$ (Ni-"zero"-alloy) was performed at the diffractometer LAD on the ISIS pulsed neutron source.

In case of the neutron experiments, the total sample scattering intensities were extracted, using the formalism of Paalman and Pings [6] for the transmission correction. Then the total sample scattering intensities were corrected for incoherent scattering, multiple scattering [7] and inelastic scattering [8], and finally the structure factors were calculated, using again the Faber-Ziman formalism.

It should be pointed out that the statistical error of the structure factors measured in Saclay was smaller

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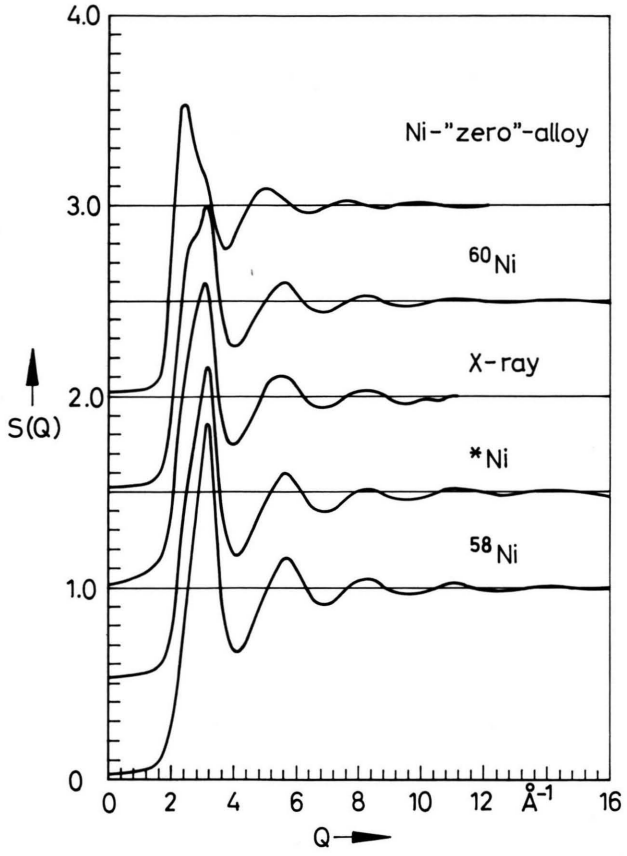

Fig. 1. Different weighted total structure factors of liquid $Ni_{33}Ge_{67}$ at 1000 °C (the labels have the following meanings: ^{58}Ni – sample with $b_{Ni} = 1.44 \cdot 10^{-14}$ cm, *Ni – sample with $b_{Ni} = 1.03 \cdot 10^{-14}$ cm, ^{60}Ni – sample with $b_{Ni} = 0.5 \cdot 10^{-14}$ cm, Ni-"zero"-alloy – sample with $b_{Ni} = 0$).

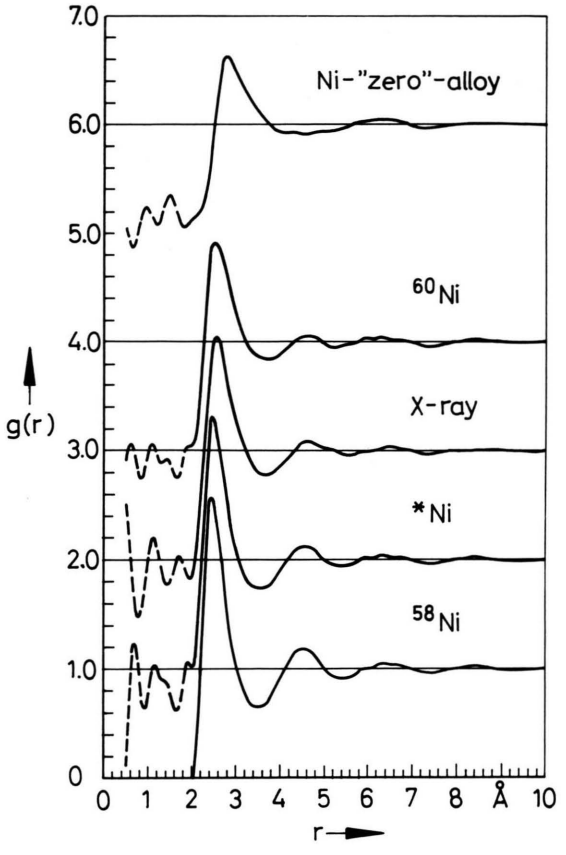

Fig. 2. Different weighted total pair correlation functions of liquid $Ni_{33}Ge_{67}$ at 1000 °C.

than 1% (caused by the high counting rate), while in the other cases it was not higher than 2%.

Except the Ni-"zero"-alloy, which has been investigated at 1000 °C only, all experiments were performed at 780 °C, 900 °C and 1000 °C.

Comparing the structure factors at different temperatures, only weak temperature dependent changes are to be seen.

Figure 1 shows the structure factors from the different experiments.

With decreasing scattering power of Ni, the shoulder at the low Q-side of the structure factor's main peak growths, and in the case of the ^{60}Ni enriched sample a prepeak appears.

The structure factor of the Ni-"zero"-alloy gives directly the part due to the Ge–Ge correlation. It is very similar to the structure factor of the pure Ge melt.

Table 1. Weighted distances of the first coordination shell.

	r^1 [Å]		
	780 °C	900 °C	1000 °C
X-ray	2.52	2.53	2.54
$*Ni_{33}Ge_{67}$	2.45	2.45	2.45
$^{60}Ni_{33}Ge_{67}$	2.49	2.49	2.50
$^{58}Ni_{33}Ge_{67}$	2.45	2.45	2.45
Ni-"zero"-alloy	–	–	2.70

For the calculation of the pair correlation functions the structure factors were interpolated to the estimated value of $S(0)$ [9].

With decreasing scattering power of Ni the main peak of the pair correlation functions becomes broader and more asymmetrical while the following peaks become weaker (Figure 2). In the case of the Ni-"zero"-alloy the peaks behind the first one are very low.

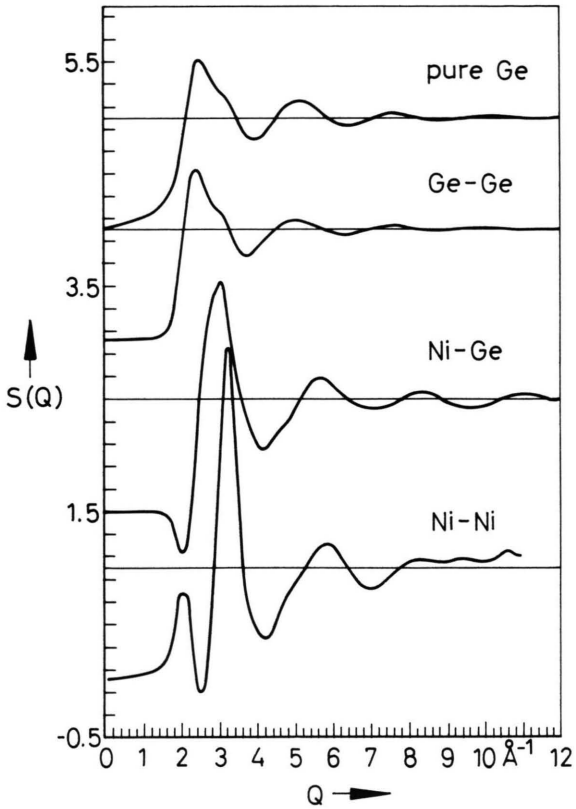

Fig. 3. Partial structure factors of liquid $Ni_{33}Ge_{67}$ at 1000 °C.

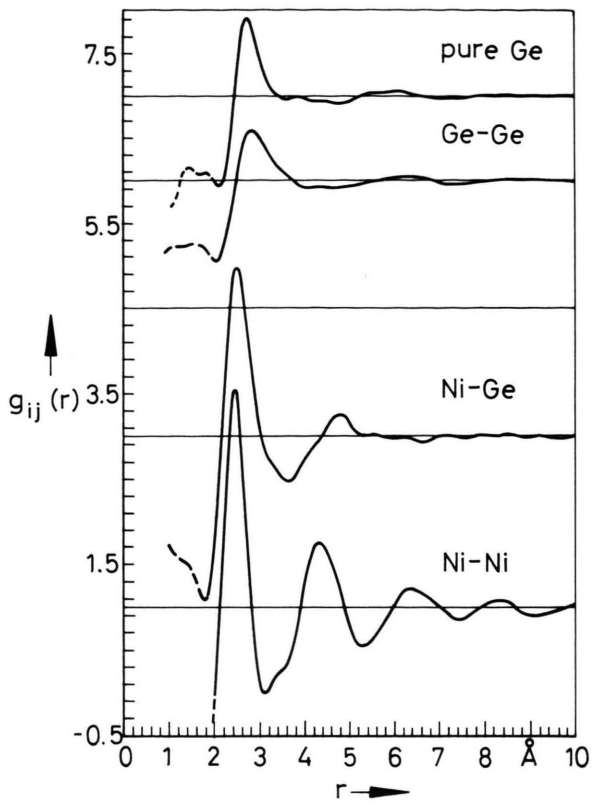

Fig. 4. Partial pair correlation functions of liquid $Ni_{33}Ge_{67}$ at 1000 °C.

Table 1 shows the neutron and X-ray weighted distance of nearest neighbours r^1 at the different temperatures. The temperature dependent changes of r^1 are very small, however r^1 tends to a smaller value if the scattering power of Ni increases.

Partial Structure Factors and Correlation Functions

The Faber-Ziman structure factor is the weighted sum of the partial one's according to

$$S(Q) = \sum_{i=1}^{2} \sum_{j=1}^{2} \frac{c_i c_j b_i b_j}{(c_i b_i + c_j b_j)^2} S_{ij}(Q), \qquad (1)$$

c_i = concentration of the atom-type i,
b_i = scattering length of the atom-type i,
Q = momentum transfer.

Three different weighted total structure factors are in principle sufficiant for the determination of the partial structure factors. In our case, at 1000 °C five different weighted total structure factors are available, the different combinations of them delivering 10 sets of equations, so that a good determination of the partial structure factors should be possible. However, the amount of the determinant of the system matrix in all cases was very small (between 0.05 and 0.0057), and only the results of those sets of equations, which include the Ni-"zero"-alloy, were usable.

Figure 3 shows the derived partial structure factors, which are averaged values of those calculated one's which were accepted to have "physically reasonable behaviour".

In the S_{Ni-Ge} a dip before the first peak can be seen; at the same position S_{Ni-Ni} possesses a maximum. This behaviour indicates, according to Enderby [10], some degree of charge transfer between the constituents.

The partial pair correlation functions (Fig. 4) show strong oscillations in the case of g_{Ni-Ni} over the whole presented r-range, while in g_{Ni-Ge} the oscillations behind the second peak nearly disappear.

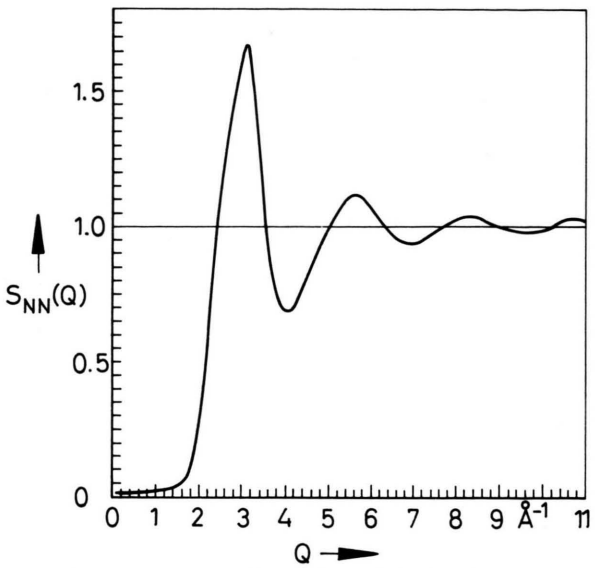

Fig. 5. Partial structure factor S_{NN} of liquid $Ni_{33}Ge_{67}$ at 1000 °C.

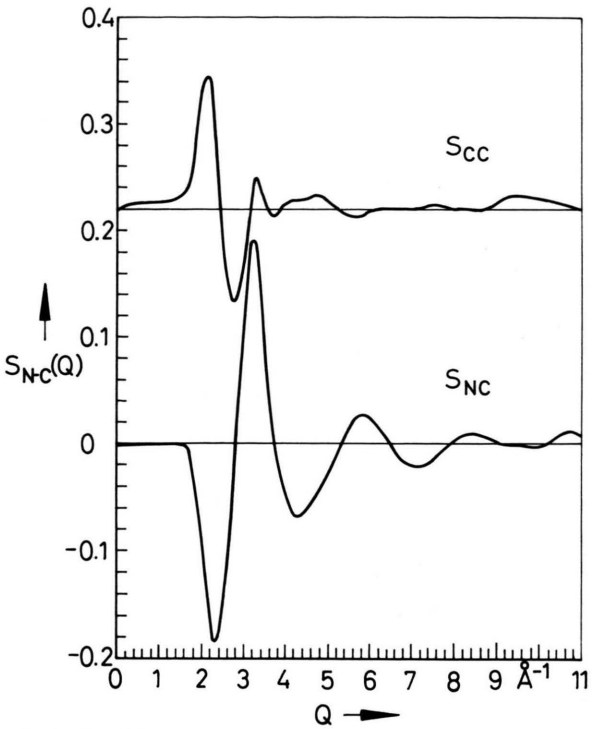

Fig. 6. Partial structure factors S_{NC} and S_{CC} of liquid $Ni_{33}Ge_{67}$ at 1000 °C.

Table 2. Partial distances and coordination numbers of the first shell (N_{Min} and N_{Sym} obtained from integration up to the first minimum and from the first shell assumed to be symmetrical).

	r^I [Å]	N_{Min}	N_{Sym}
Ni–Ni	2.44	2.6	2.7
Ni–Ge	2.48	5.9	5.2
Ge–Ni	–	2.9	2.5
Ge–Ge	2.76	4.6	6.1
pure Ge (960 °C)	2.70	6.1	4.9
pure Ni [13]	2.47	12.6	9.1

g_{Ge-Ge} shows an asymmetric first peak, broader than in the case of pure molten Ge. The higher oscillations are very weak.

The shortest distances of Ni–Ni pairs (2.44 Å) and Ni–Ge pairs (2.48 Å) are nearly the same, while the shortest Ge–Ge distance of 2.76 Å is even greater than in pure Ge melt (2.70 Å). The shortest distance of Ni–Ge pairs is shorter than the value of 2.58 Å calculated from the shortest distances in the pure melts of the constituents (Table 2), assuming simple hard spheres. The coordination numbers are also given in Table 2.

Additionally, the partial structure factors, using the Bhatia-Thornton Form [11], were estimated (Figs. 5 and 6) and the radial concentration correlation func-

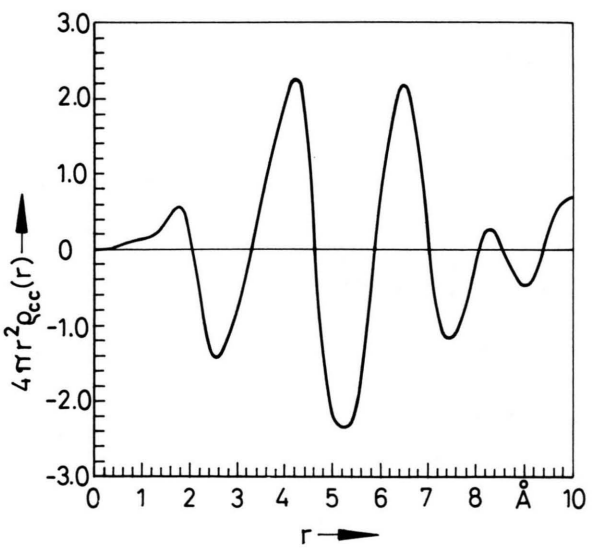

Fig. 7. Radial concentration correlation function of liquid $Ni_{33}Ge_{67}$ at 1000 °C.

tion $4\pi r^2 \varrho_{cc}(r)$ (Figure 7), introduced by Ruppersberg [12], was calculated by integration of S_{CC}. It shows a strong minimum in the same r-range where g_{Ni-Ni} and g_{Ni-Ge} have their first peak. This behaviour indicates a preferred interaction between Ni and Ge atoms in the first coordination shell.

Finally, the short-range order parameter α was calculated, using the equation

$$\alpha = \frac{\int 4\pi r^2 \varrho_{CC}(r)\, dr}{\int 4\pi r^2 \varrho_{NN}(r)\, dr}, \qquad (2)$$

where $4\pi r^2 \varrho_{NN}(r)$ results from Fourier transformation of S_{NN}. The integration over the first coordination shell gives $\alpha = -0.15$. This again indicates a preferred correlation of unlike atoms in the first shell. The degree of chemical short-range order is

$$\frac{\alpha}{\alpha_{max}} = \frac{-0.15}{-0.50} = 30\%.$$

Conclusion

The distance of Ni–Ge pairs, shorter than in the case of simple hard spheres, the strong minimum in $4\pi r^2 \varrho_{CC}(r)$ in the region of the first coordination shell and the value of the short-range order parameter indicate chemical short-range ordering. The qualitative behaviour of the partial functions S_{Ge-Ge} and g_{Ge-Ge} emphasizes a structural order of the Ge atoms which is similar to that of the pure Ge melt.

Therefore, it is assumed that in the eutectic melt two types of structural order occur: At first, an arrangement of Ge and Ni atoms with preferred interaction between them and surprisingly showing charge transfer and, secondly, an arrangement of the remaining Ge atoms similar to that in the pure Ge melt.

Acknowledgement

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[1] T. B. Massalski, J. L. Murray, L. H. Bennet, and H. Baker, Binary alloy phase diagrams, Vol. 2, American Society for Metals, Ohio 1986.
[2] V. A. Shovskii, V. P. Kazimirov, V. E. Sokol'skii, and G. I. Batalin, Ukr. Fiz. Zh. (Russ. Ed.) **27,** 1545 (1982).
[3] V. P. Kazimirov, Thesis, Tscheljabinsk, 1991.
[4] W. Hoyer, E. Thomas, and M. Wobst, Kristall und Technik **15,** 903 (1980).
[5] T. E. Faber and J. M. Ziman, Phil. Mag. **11,** 153 (1965).
[6] H. H. Paalman and C. J. Pings, J. Appl. Phys. **33,** 2635 (1962).
[7] V. F. Sears, Adv. Phys. **24,** 1 (1975).
[8] G. Placzek, Phys. Rev. **86,** 377 (1952).
[9] H. Neumann, W. Matz, and W. Hoyer, Exp. Technik Phys. **36,** 105 (1988).
[10] J. E. Enderby, J. Phys. C: Solid State Phys. **15,** 4609 (1982).
[11] A. B. Bhatia and D. E. Thornton, Phys. Rev. **B 2,** 3004 (1970).
[12] H. Ruppersberg and H. Egger, J. Chem. Phys. **63,** 4095 (1975).
[13] N. Schmitz-Prange and R. Kohlhaas, Z. Naturforsch. **25a,** 1752 (1970).