Structure of Mn\textsubscript{40}Zn\textsubscript{60} liquid alloy

D Es Sbihi, B Grosdidier and J G Gasser

Laboratoire de Physique des Milieux Denses,
Institut de Chimie Physique et Matériaux, Université Paul Verlaine - Metz.
1 Bd Arago 57078 METZ Cedex 3 France.

E-mail: grosdidi@univ-metz.fr

Abstract. In this work we present the structural study of the Mn\textsubscript{40}Zn\textsubscript{60} liquid alloy, whose two components have a high vapour pressure. The structure has been measured by neutron diffraction. The investigation of the chemical order in this alloy was readily made possible. This is due to the manganese negative scattering length which allows a good contrast. A magnetic correction has been considered since manganese is paramagnetic in the liquid state. An “effective” spin is obtained and its value is discussed. The interpretation of the atomic structure is done in the frame of the Bhatia-Thornton formalism, \((S_{NN}(q), S_{NC}(q), S_{CC}(q))\) which allows to separate topological, size and chemical effects. It appears clearly that manganese ions and zinc ions have approximately the same radius in the alloy as \(S_{NC}(q) \approx 0\).

The Bhatia-Thornton number-number partial structure factor \(S_{NN}(q)\) has been approximated by a linear combination of the experimental structure factors of the two alloy pure components. In the frame of this assumption, the Bhatia-Thornton concentration-concentration partial structure factor \(S_{CC}(q)\) is obtained, and shows clearly that this alloy is hetero-coordinated. The hard sphere model cannot explain the structure of this alloy. Its behaviour is compared to other manganese-polyvalent alloys and the general trends are discussed.

Keys words: Liquid Alloys, Neutron Scattering, Short Range Order, Manganese, Zinc.

1. Introduction

In order to understand the physical properties of manganese alloys such as electrical properties, we present here structural results concerning the Mn\textsubscript{40}Zn\textsubscript{60} liquid alloy. Manganese is one of scarce metals which possess a negative scattering length leading to a great contrast [1]. This latter aspect is crucial for the determination of chemical order in the alloy. The interpretation of the structure is done in the frame of the Bhatia-Thornton formalism [2] \((S_{NN}(q), S_{NC}(q), S_{CC}(q))\) which allow to separate topological, size and chemical effects. We measured by neutron diffraction the structure factor of Mn\textsubscript{40}Zn\textsubscript{60} at 900 °C on the two axis spectrometer 7C2 built on the hot source of the LLB\textsuperscript{1}’s Orphée reactor at Saclay. The two components of this alloy have a very high vapour pressure making the experiment readily difficult. A magnetic correction has been taken into account due to the fact that liquid manganese is paramagnetic. This correction allows calculating a value for the effective spin of

\textsuperscript{1} Laboratoire commun (LLB) CEA-CNRS
manganese in the alloy. In ‘section 2’, we present the Bhatia-Thornton and the Faber-Ziman formalisms which are necessary to the study of this structure, the relations between the alloy total structure factor and the partial structure factors and the relations between partial structure factors \( a_i(q) \) and partial pair correlation functions \( g_{ij}(r) \). The experimental set-up and the magnetic scattering correction method are described in ‘section 3’. In ‘section 4’, we show how we can obtain the partial structure factors \((S_{NN}(q), S_{NC}(q), S_{CC}(q))\) and their corresponding pair correlation functions. The Warren chemical short-range order parameter \([3]\) and the degree of hetero-coordination are estimated and discussed in ‘section 5’ before drawing a general conclusion.

The total structure factor \( S(q) \) of an alloy is related to three sets of partial structure factors: the Ashcroft-Langreth \([4]\), the Faber-Ziman \([5]\) and the Bhatia-Thornton \([2]\) partial structure factors. The relations between them are given by Waseda \([6]\). In this work, we only use the Bhatia-Thornton and Faber-Ziman formalisms. The total structure factor is related to the Bhatia-Thornton partial structure factors \( S_{NN}(q) \), \( S_{NC}(q) \) and \( S_{CC}(q) \) by:

\[
S(q) = w_{NN}S_{NN}(q) + w_{NC}S_{NC}(q) + w_{CC}S_{CC}(q)
\]

(1)

where the weight factors are written versus the concentrations \( c_1, c_2 \) and the neutron scattering lengths \( b_1, b_2 \) by:

\[
w_{NN} = \frac{(c_1 b_1 + c_2 b_2)^2}{c_1 b_1^2 + c_2 b_2^2}, \quad w_{NC} = \frac{2 (c_1 b_1 + c_2 b_2) (b_1 - b_2)}{c_1 b_1^2 + c_2 b_2^2} \quad \text{and} \quad w_{CC} = \frac{(b_1 - b_2)^2}{c_1 b_1^2 + c_2 b_2^2}
\]

(2)

The Bhatia-Thornton partial structure factors have each a clear physical meaning. The partial structure factors \( S_{NN}(q) \), \( S_{NC}(q) \) and \( S_{CC}(q) \) indicate respectively the topological, the size and the chemical effects. They are expressed as functions of the Faber-Ziman partial structure factors \( a_i(q) \) \((i, j = 1, 2)\) by:

\[
S_{NN}(q) = c_1^2 a_{11}(q) + 2c_1 c_2 a_{12}(q) + c_2^2 a_{22}(q)
\]

(3)

\[
S_{NC}(q) = c_1 c_2 [c_1 (a_{11}(q) - a_{12}(q)) - c_2 (a_{22}(q) - a_{12}(q))]
\]

(4)

\[
S_{CC}(q) = c_1 c_2 [c_1 (a_{11}(q) + a_{22}(q) - 2a_{12}(q))]
\]

(5)

The Faber-Ziman partial structure factors \( a_i(q) \) are connected to the partial pair correlation functions \( g_{ij}(r) \) by:

\[
g_{ij}(r) - 1 = h_{ij}(r) = \frac{1}{2\pi^2 \rho_0^2} \int_0^\infty \rho(q)(a_i(q) - 1)\sin(qr) \ dq
\]

(6)

where \( \rho_0 \) is the average number density.

The fact that the Bhatia-Thornton partial structure factors have clear physical meanings allows putting forward several assumptions for the study of the manganese-zinc alloy. In case of hetero-coordination, the chemical effect appears in the partial structure factors \( a_{11}(q) \) and \( a_{22}(q) \) by a positive prepeak and by a negative prepeak in \( a_{12}(q) \). The prepeaks cancel in \( S_{NN}(q) \) and in \( S_{NC}(q) \) but are magnified in \( S_{CC}(q) \). If the two species have very close sizes in the alloy then \( S_{NC}(q) \) may be approximately zero. If the size of the components ions do not change in the alloy then it is possible to replace \( S_{NN}(q) \) by a linear combination of the structure factors \( S_i(q) \) and \( S_2(q) \) of the two pure metals:

\[
S_{NN}(q) \approx c_1 S_1(q) + c_2 S_2(q)
\]

(7)

These different assumptions lead to consider that the chemical effect appears mainly in the partial structure factor \( S_{CC}(q) \). The Fourier transform of \( S_{CC}(q)/(c_1 c_2) \) is given by:

\[
\frac{1}{2\pi^2 \rho_0^2} \int_0^\infty \frac{q(S_{CC}(q) - 1)\sin(qr)}{c_1 c_2} \ dq = g_{11}(r) + g_{22}(r) - 2g_{12}(r) = \frac{g_{CC}(r)}{(c_1 c_2)^2}
\]

(8)
The quantity \( g_{11}(r) + g_{22}(r) - 2g_{12}(r) \) is linked to the difference between the homo-coordination, characterized by \( g_{11}(r) + g_{22}(r) \) and the hetero-coordination characterized by \( 2g_{12}(r) \) and indicates the nature of the chemical order in the first nearest neighbours shell. The respective coherent scattering lengths \([7]\) of manganese and zinc are respectively equal to \(-3.73\text{ fm}\) and \(+5.68\text{ fm}\), the weights \( w_{NN}\), \( w_{NC}\) and \( w_{CC}\) are respectively equal to \(0.147\), \(1.774\) and \(3.553\). The contrast is defined by the equation:

\[
C = 1 - w_{NN} = c_1c_2w_{CC} \quad (9)
\]

For the \(\text{Mn}_{40}\text{Zn}_{60}\) alloy, it is equal to 0.86 and is close to its maximum value (unity). The study of the scarce alloys containing a metal with negative scattering length presents a very strong interest and has been used for liquid alloys with lithium \([8]\). The situation is more complicated for manganese, because manganese has also a magnetic scattering cross section.

3. Experimental set-up and corrections

A complete description of the 7C2 spectrometer can be found in reference \([9]\). We only recall the main characteristics. The neutron beam section is equal to \(5 \cdot 2\text{ cm}^2\). The scattering wave vector is in the range \(0.3-16\text{ Å}^{-1}\), the experimental wavelength is \(\lambda = 0.701\text{ Å}\). The angular resolution is equal to \(0.2°\). The number of detectors is 640. The highest neutron flux value is \(2 \cdot 10^7\text{ neutrons cm}^{-2}\text{ s}^{-1}\) at \(\lambda @ 0.7\text{ Å}\). The different alloys have been elaborated with metals of purity close to \(99.999\%\). The liquid alloy is put in an amorphous silica cell which is placed in a vacuum furnace up to a temperature of \(900\text{ °C}\). The corrections for background, furnace, empty container effects, self-absorption, multiple scattering, inelastic scattering and incoherent scattering contributions are done following the procedure described elsewhere \([10]\). The quality of these corrections is estimated by using a vanadium rod, which presents the same geometric characteristics than the sample namely a cylinder with a height of \(60\text{ mm}\) and a diameter of \(8\text{ mm}\). The result of these corrections is presented in ‘figure 1’. The experimental differential cross section \(\frac{d\sigma}{d\Omega}\) presents a characteristic shape of a magnetic scattering contribution attributed to paramagnetic scattering from the manganese ions. Thus a magnetic correction must be done considered. It consists in a subtraction of the paramagnetic cross section given by the usual formula \((7.33)\) of the reference \([11]\):

\[
\frac{d\sigma_{\text{pol}}}{d\Omega} = \frac{2\pi}{3}S(S+1) \left(\frac{e^2}{mc^2}\right)^2 \left(\frac{g}{2} f_{sd}(q)\right)^2 \quad (10)
\]

where the magnetic form factor \(f_{sd}(q)\) may be written by the ‘equation (7.28)’ of the reference \([11]\):

\[
f_{sd}(q) = \frac{1}{g} \left( \frac{g_s}{g} + \frac{g}{g} \right) \quad (11)
\]

The numbers \(g_s\) and \(g\) are the spin gyromagnetic ratio and the Landé splitting factor respectively. The \(\tilde{J}_i\) functions are the radial integrals for the \(d\) electrons and are tabulated in reference \([12]\) in an approximate form given by:

\[
\tilde{J}_i(s) = A \exp(-as^2) + B \exp(-bs^2) + C \exp(-cs^2) + D \quad (12)
\]

where \(s = q/(4\pi)\). The parameters of \(f_{sd}(q)\) are those of the \(\text{Mn}^{2+}\) ion (spin momentum \(S=2.5\), orbital momentum \(L=0\) and total momentum \(J=2.5\)). We have:

for \(\tilde{J}_0\): \(A = 0.4220\), \(a = 17.6840\), \(B = 0.5948\), \(b = 6.0050\), \(C = 0.0043\), \(c = -0.6090\), \(D = -0.0219\),

for \(\tilde{J}_2\): \(A = 2.0515\), \(a = 15.5561\), \(B = 1.8841\), \(b = 6.0625\), \(C = 0.4787\), \(c = 2.2323\), \(D = 0.0027\).
With these numerical values $\frac{d\sigma_{\text{Mn}}}{d\Omega}$ is equal to 1.701 barn, which is very greater than 0.284 barn.

The magnetism of the alloy results from manganese. The quantity $\frac{d\sigma_{\text{Mn}}}{d\Omega}$ must be multiplied by the manganese atomic concentration $c_1$ and by a correction term $c_{\text{eff}}$. The corrected experimental structure factor $S_{\exp}(q)$ is obtained by the formula:

$$
S_{\exp}(q) = \frac{d\sigma}{d\Omega} \frac{c_{\text{eff}} c_1 d\sigma_{\text{Mn}}}{c_1 b_1^2 + c_2 b_2^2}
$$

The value of $c_{\text{eff}}$ is obtained by realizing the condition [6]:

$$
\int_0^{q_{\text{MAX}}} q^2 (S_{\exp}(q) - 1) dq = -2\pi^2 \rho w_{NN}
$$

The result is 0.405.

**Figure 1.** Experimental total (dashed line), nuclear (full line) and magnetic (dashed and dotted line) differential cross sections for the Mn$_{40}$Zn$_{60}$ at 900 °C. The curves are extrapolated at low $q$ values ($q \leq 0.7$ Å$^{-1}$).

This value of $c_{\text{eff}}$ gives a consistent value, close to zero, of the Fourier transform at $r=0$. Considering the magnetic correction, the total error on $S_{\exp}(q)$ is estimated to be 10% for $0.8 < q < 5$ Å$^{-1}$ and nearly 2% for $q > 5$ Å$^{-1}$. This comes from the $q^2$ term in ‘equation (14)’. This leads to an estimated total error near 5% on the total pair correlation function $g(r)$. The magnetic correction affects the pair correlation function only between 0 and 1.8 Å, thus it has no influence on the discussion about the atomic structure of this alloy. This correction allows us to calculate a mean effective spin of manganese ion in this liquid alloy by the relationship:

$$
S_{\text{eff}} (S_{\text{eff}} + 1) = c_{\text{eff}} S (S + 1)
$$

which leads to $S_{\text{eff}}$ approximately equal to $1.4 \pm 0.1$, due to Kondo effect [13]. This spin behaviour has even been observed by Simonet et al. [14] in Al-Pd-Mn liquid alloys. Their calculated spin values of manganese ions are comparable to ours (1.3 at 1180 K).
4. Results

The total experimental structure factor $S_{\text{exp}}(q)$ is displayed in ‘figure 2’. Two peaks can be clearly observed. The first one, located at $1.95 \, \text{Å}^{-1}$, may be assigned to $S_{\text{CC}}(q)$ and the second one, located at $2.95 \, \text{Å}^{-1}$, to $S_{\text{NN}}(q)$. The position of the second peak is very close of those of the pure components peaks.

![Figure 2](image)

**Figure 2.** Experimental total structure factor $S_{\text{exp}}(q)$ (dashed and dotted line) obtained from the experiment. Linear combination (dashed line) of the pure metal experimental structure factors [6]. The full line corresponds to the reduced Bhatia Thornton ($S_{\text{CC}}(q)/(c_1c_2)$) partial structure factor for $\text{Mn}_{40}\text{Zn}_{60}$ at $900 \, ^\circ\text{C}$.

These positions are given by Waseda [6]. The pure manganese and zinc experimental main peaks are respectively located at $2.85 \, \text{Å}^{-1}$ and $2.90 \, \text{Å}^{-1}$. The narrowness of the second peak leads us to assume that the manganese ions and the zinc ions have very close size in the alloy ($S_{\text{NN}}(q) \approx 0$). ‘Figure 2’ shows also the structure $S_{\text{lin}}(q)$ of the alloy in the frame of the assumption: $[S_{\text{lin}}(q) = w_{\text{NN}}(S_{\text{NN}}(q) - 1) + 1]$. The quantity $S_{\text{CC}}(q)/(c_1c_2)$ is obtained from the experimental structure factor $S_{\text{exp}}(q)$ by the equation:

$$
\frac{S_{\text{CC}}(q)}{c_1c_2} \approx \frac{1}{c_1c_2w_{\text{CC}}}[S_{\text{Exp}}(q) - w_{\text{NN}}(c_1S_1(q) + c_2S_2(q))]
$$

(15)

and is also displayed in ‘figure 2’. The height of the main peak is equal to 1.25. It proves that this alloy is hetero-coordinated. We compare the experimental and hard sphere structure factors. For both metals, the hard sphere diameters $\sigma_{ii}$ in the alloy are taken to be those of pure metals $\sigma_i$, which have been deduced from the experimental packing fraction and from the experimental density. The packing fraction is given by Waseda [6] as a function of temperature: $\eta_i = A_i \exp(-B_i/T)$, (the parameters $A_i$ and $B_i$ have been tabulated in ‘table 3-1’ of Waseda's book). The density is compiled by Crawley [15] as a function of temperature under the form: $d_i = a_i - b_i(T - T_{Mi})$, $T_{Mi}$ is the melting temperature of the $i$th pure metal. The hard sphere diameters of pure manganese and zinc in the alloy are respectively:
\( \sigma_{\text{Mn}} = 2.42 \text{ Å}, \ \sigma_{\text{Zn}} = 2.40 \text{ Å} \) at 900 °C. The “hard sphere alloy” is quasi an ideal mixture which leads to \( S_{CC}(q) \approx c_1 c_2 \) for all \( q \) values. It will not be displayed. The peak of \( S_{CC}(q)/(c_1 c_2) \) (height 1.25 at 1.85 Å\(^{-1}\)) indicates a weak chemical interaction confirming that the hetero-coordination is less pronounced than in \( \text{Mn}_{60}\text{Sb}_{40} \) (height 2.30 at 1.775 Å\(^{-1}\)) \[16\] and \( \text{Mn}_{69}\text{Ge}_{31} \) (height 2.00 at 1.95 Å\(^{-1}\)) \[17\] liquid alloys. In ‘figure 3’, the pair correlation functions are shown. The function \( g_{\text{exp}}(r) \) is obtained by Fourier transform of the experimental structure factor \( S_{\text{exp}}(q) \). The function \( g_{\text{lin}}(r) = w_{\text{NN}}(g_{\text{NN}}(r) - 1) + 1 \) is obtained by Fourier transform of \( (c_1 S_1(q) + c_2 S_2(q)) \). The two curves are in phase for \( r \geq 7.5 \text{ Å} \). It confirms that the ions retain their size in the alloy.

**Figure 3.** Pair correlation functions obtained from the experiment calculated for the \( \text{Mn}_{40}\text{Zn}_{60} \) at 900 °C (corresponds to the figure 2 experimental structure factor with the same symbols).

In the real space, the effect of the chemical order is only located in the \( r \) range \( 2<r<6 \text{ Å} \). In ‘figure 3’, the function \( g_{CC}(r) + 1 \) is also presented \( (g_{CC}(r) \) is deduced from ‘equation (8)’). This function has been extracted from the alloy total pair correlation function \( g_{\text{exp}}(r) \) and from the function \( g_{\text{lin}}(r) \) by equation:

\[
g_{CC}(r) \approx \frac{g_{\text{exp}}(r) - g_{\text{lin}}(r)}{w_{CC}}
\]

This function indicates either the homo-coordination if it is positive or the hetero-coordination if it is negative in the first neighbours shell. The hetero-coordination appears weakly in the short interatomic distance range \((2.5, 3.2 \text{ Å})\). Its minimum value is -0.063 at \( r \) equal 2.70 Å. For \( r \geq 6 \text{ Å} \), the curve presents some very small oscillations. It is possible to consider, taking account the experimental error, that after this distance, the alloy is fully disordered. The estimated value of the Warren chemical short–range order parameter \[1,3,18\] (calculated, at the minimum of \( g_{\text{NN}}(r) \) 3.6 Å) is equal to -0.032 and the degree of hetero-coordination is approximately 5%. This value confirms the weak hetero-coordination of this alloy.
5. Discussion
The first peak of the experimental structure factor at 1.95 Å⁻¹ is a proof of a chemical order in this alloy. From the Sargent-Welch table of properties of the elements [20], the ionic character of this alloy is very small, only of 0.5%, with a difference of electronegativities of 0.1. A charge transfer between manganese to zinc leading to a variation of the hard sphere diameter is near of zero. This is firstly checked by the behaviour of the oscillations for r ≈ 7.5 Å and secondly checked by the Ben Abdellah’s resistivity measurements [21] done in our laboratory for the, $\text{Mn}_{0.05}\text{Zn}_{0.95}$, $\text{Mn}_{0.10}\text{Zn}_{0.90}$, $\text{Mn}_{0.15}\text{Zn}_{0.85}$, $\text{Mn}_{0.20}\text{Zn}_{0.80}$ and $\text{Mn}_{0.30}\text{Zn}_{0.70}$ alloys at 850 °C. These measurements allow us to estimate an extrapolated value (115 $\mu \Omega \cdot \text{cm}$) of the resistivity for $\text{Mn}_{0.40}\text{Zn}_{0.60}$ at 850 °C. This value is close to the interpolated (103 $\mu \Omega \cdot \text{cm}$) value of the pure component resistivities. Furthermore, the value of the resistivity ρ corresponds to a metallic behaviour ($\rho < 330 \mu \Omega \cdot \text{cm}$) following the criteria based on difference of the electron energy work functions ($\Delta \Phi < 1.2 \text{ eV}$) and developed by W van der Lugt and W Geertsma [22]. The difference of the work function of zinc and manganese [23] ($\Delta \Phi = \Phi_{\text{Zn}} - \Phi_{\text{Mn}} = 0.13 \text{ eV}$). The alloy does not present an ionic character corresponding to a much greater resistivity (like Li-Pb [24]). The weak chemical order is also checked by the fact that the structure factor $S_{\text{CC}}(q)/(c_1 c_2)$ of this alloy is lower than the unity (0.81). The energy work function difference is greater than of substitution [1] liquid alloy Li-Ca ($\Delta \Phi = 0.03 \text{ eV}$ [23] with electronegativities difference equal to zero [21]).

6. Conclusion
We have presented our experimental results of neutrons scattering on molten manganese-zinc alloy. The determination of the magnetic scattering cross section gives a magnetic effective spin of manganese (1.4) in the liquid alloy, very different from the theoretical one (≈ 2.5). We show that this alloy is weakly hetero-coordinated. The hard sphere model cannot explain this structure. An ionic character is excluded by the value of the resistivity [21] and by the behaviour of the total pair correlation function at large distances. Complementary X-ray measurements of the structure of this liquid alloy would support our conclusions.

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