STUDY OF LIQUID NICKEL-VANADIUM ALLOYS BY NEUTRON DIFFRACTION AND MODEL SIMULATION

J. Lemarchand, J. Bletry, P. Desre

► To cite this version:

J. Lemarchand, J. Bletry, P. Desre. STUDY OF LIQUID NICKEL-VANADIUM ALLOYS BY NEUTRON DIFFRACTION AND MODEL SIMULATION. Journal de Physique Colloques, 1980, 41 (C8), pp.C8-163-C8-166. 10.1051/jphyscol:1980842 . jpa-00220348

HAL Id: jpa-00220348

<https://hal.science/jpa-00220348>

Submitted on 1 Jan 1980

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

STUDY OF LIQUID NICKEL-VANADIUM ALLOYS BY NEUTRON DIFFRACTION AND MODEL SIMULATION

J.L. Lemarchand, J. Blettry and P. Desre

Laboratoire de Thermodynamique et Physico-Chimie Métallurgiques, ENSEEG, B.P. 44, 38401 Saint Martin d'Hères, France.

1. INTRODUCTION

Structure factor determination is one of the main purposes of diffraction experiments on liquid or amorphous metals. In the case of binary alloys, a combination of three independent measurements is needed to obtain the three partial structure factors. However, these determinations are very delicate and their accuracy is often limited.

Much more accurate, although less complete, information is obtained from one single diffraction measurement. In that case, comparison with model calculation can lead to a quantitative interpretation.

In this paper, neutron diffraction experiments on vanadium-X alloys are presented which allow the partial structure factor of X-X pairs to be determined. Nickel-Vanadium alloys are studied in order to investigate chemical ordering effects into the liquid phase around the eutectic composition [1]. Experimental results are finally interpreted with the aid of geometrical models [2].

2. PRINCIPLE OF THE EXPERIMENTS

The differential cross-section for coherent scattering by a binary alloy may be written :

$$\frac{d\sigma}{d\Omega}^{\text{coh}} = \sum_1^2 (c_i c_j)^{1/2} b_i b_j S_{ij}(Q) \quad (1)$$

or in a normalized form* :

$$S(Q) = \frac{d\sigma}{d\Omega}^{\text{coh}} / \sum_1^2 c_i b_i^2 \quad (2)$$

In these expressions, c_i and b_i are respectively the atomic concentration and the coherent nuclear scattering length of element i ,

* which goes to 1 for large Q

2θ is the scattering angle, λ the neutron wavelength, $Q = 4\pi \frac{\sin\theta}{\lambda}$ the modulus of the scattering vector and the Ashcroft-Langreth partial structure factors are defined by [3] :

$$S_{ij}(Q) = \delta_{ij} + \rho (c_i c_j)^{1/2} \int [P_{ij}(r) - 1] e^{i\vec{Q}\cdot\vec{r}} d_3r$$

where : δ_{ij} is the Kronecker δ function

. $\rho = \frac{N}{V}$ the number density and

. $P_{ij}(r)$ the normalized distribution function of i - j pairs.

In the case of nickel-vanadium alloys where the scattering length of nickel : $b_1 = 1.03 \cdot 10^{-12} \text{ cm}$ is much larger than the scattering length of vanadium : $b_2 = -0.051 \cdot 10^{-12} \text{ cm}$, a single diffraction experiment gives directly the nickel-nickel structure factor $S_{11}(Q)$ since coherent cross-section (1) reduces to : $\frac{d\sigma}{d\Omega}^{\text{coh}} \approx c_1 b_1^2 S_{11}(Q)$ (3). Departures from approximation (3) mainly arise from the term $(c_1 c_2)^{1/2} b_1 b_2 S_{12}(Q)$ which does not exceed 10 % of the coherent cross section if nickel concentration is greater than 0.50.

3. EXPERIMENTAL CONDITIONS

Alloys were prepared by induction melting from 0.99999 nickel and 0.990 vanadium whose oxygen content was less than 100ppm. The oxygen content of the alloys after 10 hour neutron scans was about 1000ppm. Four alloys were studied with concentrations in nickel : $c_1 = 1.00, 0.887, 0.554$ and 0.461 surrounding the eutectic composition : $c_1^e = 0.49$.

Neutron diffraction experiments were carried out at the D4 spectrometer of the Institut Laue-Langevin. A $0.693 \text{ \AA}$ wavelength was used in order to

reach a maximum Q value of $14.5 \text{ \AA}^{-1}$ which enables a good normalization of experimental scattering patterns.

The samples were cylindrical, 6 mm in diameter and 3 cm high. They were heated between 1300 and 1600°C under 10^{-5} Torr. For this purpose a high temperature furnace covering the range $800\text{--}2000^\circ\text{C}$ was built using the techniques developed at INPG laboratory [4]. For the passage of the primary beam, windows were cut in the tungsten heating element and in the thermal screens. Sapphire containers were used, resulting in a very low neutron background. These sapphire singlecrystals were oriented with a molybdenum goniometric table in order to limit the number of Bragg reflexions superposed on the liquid alloy pattern. The temperature was measured to $\pm 5^\circ\text{C}$ with an optical pyrometer.

4. DATA TREATMENT

Cross section $\frac{d\sigma}{d\Omega}$ was derived from diffraction measurements after a data treatment process which can be divided into two steps [5], [1]. The number of neutrons $C(Q)$ scattered by the alloy is first derived from experimental countings with the aid of background, container scattering and absorption corrections [6]. From $C(Q)$ one then calculates

$$\frac{d\sigma}{d\Omega} \text{ or its normalized form (which goes to 1 for large } Q): \mathcal{V}(Q) = \frac{d\sigma}{d\Omega} / \sum_{i=1}^2 c_i b_i^2 \quad (4)$$

This second step involves calculating a normalization constant [5] and correcting for multiple [7], incoherent and inelastic scattering [8]. The final cross section $\frac{d\sigma}{d\Omega}$ is the sum of the desired coherent cross section and a magnetic scattering term :

$$\frac{d\sigma}{d\Omega} = \frac{d\sigma}{d\Omega}^{\text{coh}} + \frac{d\sigma}{d\Omega}^{\text{Mag}} \quad (5)$$

5. MAGNETIC SCATTERING

5.1 - LIQUID NICKEL

In the case of pure nickel and for small Q values (i.e. around $0.3 \text{ \AA}^{-1}$), $\frac{d\sigma}{d\Omega}$ was found

equal to : 0.21 barn/sr while the coherent cross section calculated from the Ornstein-Zernike relation [9] only amounts to 0.03 barn/sr . The remaining magnetic cross section : $\frac{d\sigma}{d\Omega}^{\text{Mag}} \approx 0.18 \text{ barn/sr}$ is thus larger than the ideal paramagnet value : $\frac{d\sigma}{d\Omega}^{\text{Para}} = 0.08 \text{ barn/sr}$ calculated from Halpern and Johnson formula [10]. The difference between $\frac{d\sigma}{d\Omega}^{\text{Mag}}$ and $\frac{d\sigma}{d\Omega}^{\text{Para}}$ which has been previously observed and interpreted by Weber [11] arises from magnetic correlations in the melt. It is unfortunately impossible to obtain the magnetic correlation length from an Ornstein-Zernike plot [12] in the Q interval : $0.3 \rightarrow 1.5 \text{ \AA}^{-1}$.

On the other hand the magnetic cross section decreases with Q and becomes negligible with respect to the nuclear coherent cross section ($\approx b_1^2$) beyond $Q \approx 1.5 \text{ \AA}^{-1}$.

5.2 - NICKEL-VANADIUM ALLOYS In Ni-V alloys, the magnetic contribution to cross section (5) very likely decreases with vanadium concentration but still explains why in the 88.7at% nickel alloy experimental values of $\mathcal{V}(Q)$ are larger than calculated values of $S(Q)$ for $Q < 1.5 \text{ \AA}^{-1}$ (see figures 1 and 2).

6. PARTIAL NICKEL-NICKEL STRUCTURE FACTOR

For $Q > 1.5 \text{ \AA}^{-1}$ three main changes may be noticed on $S_{11}(Q)$ ($\approx \mathcal{V}(Q)$) as nickel concentration decreases (see figure 1) :

- i) a slight shift of the position Q_1^{11} of $S_{11}(Q)$ first peak towards small Q , arising from size effects
 - ii) an overall decrease of $S_{11}(Q)$ oscillations which is due to the decrease of the partial number density of nickel : $\rho_1 = c_1 \rho$
 - iii) the progressive appearance of a prepeak around $Q \approx 1.9 \text{ \AA}^{-1}$ arising from a chemical order effect.
- This prepeak which is reduced to a shoulder in the 88.7 at % nickel alloy transforms into a well resolved peak in 55.4 and 46.1 at % nickel alloys.

Fig. 1 - Experimental $S(Q)$.
 $T=1500^{\circ}\text{C}$, $C_1=1$. (a), 0.887 (b), 0.554 (c).

In the next section all these results are quantitatively interpreted.

7. MODEL INTERPRETATION AND CONCLUSIONS

7.1 SIZE EFFECT

If one neglects the coupling between chemical order and size effects and if atomic diameters are additive Q_1^{11} is related to atomic diameters d_1 and d_2 by [2] :

$$Q_1^{11} = \frac{1}{d_1} [7.55 - 4.3 (\bar{d} - 1)] \quad (6)$$

where $\bar{d} = c_1 d_1 + c_2 d_2$ is the average atomic diameter of the alloy. Experimental Q_1^{11} values agree with relation (6) to a 1 % accuracy if we take for

Fig. 2 - Calculated $S(Q)$. $T=1500^{\circ}\text{C}$,
 $T=1500^{\circ}\text{C}$, $C_1=1$. (a'), 0.887 (b'), 0.554 (c')

d_1 and d_2 the Goldschmidt diameters of Ni and V :

$d_1 = 2.50$ and $d_2 = 2.72 \text{ \AA}$. Therefore atomic diameters of nickel and vanadium seem to be additive and almost insensitive to alloying.

TABLE I

Parameters of the fit	ρ^* ($\text{At}/\text{\AA}^3$)	ρ_m ($\text{At}/\text{\AA}^3$)	d_m ($\text{\AA}$)	ξ ± 0.04
Nickel at %				
1.00	0.0806	0.0712	2.50	-
0.887	0.0793	0.0605	2.51	-0.10
0.554	0.0756	0.0564	2.54	-0.12

* These values are obtained from a linear interpolation between measured densities of liquid nickel and vanadium.

7.2 CHEMICAL ORDER

Measured $\chi(Q)$ can be fitted with a good accuracy (see figures 1 and 2) by calculated $S(Q)$ using relation [2]:

$$S_{ij}(Q) = \delta_{ij} + \exp(-\sigma^2 Q^2) \frac{\rho}{\rho_m} [S_{ij}^{HS}(Q) - \delta_{ij}] \quad (7)$$

Let us consider the different terms of this equation. The Debye-Waller factor which is introduced in (7) to fit the damping of $\chi(Q)$ oscillations is related to some mean vibration frequency ν by:

$$\sigma^2 = \frac{h}{8\pi^2 m \nu} \coth\left(\frac{h\nu}{2k_B T}\right) \quad (8)$$

where h is the Planck constant, k_B the Boltzmann constant and m the mean atomic mass of the alloy. It turns out that ν equals 5.10^{12} s^{-1} i.e. roughly 2/3 of the mean Debye frequency of the corresponding crystalline phases, in agreement with our previous model for liquid metals [15].

Partial structure factors $S_{ij}^{HS}(Q)$ are calculated from our geometrical model [2]. If one again neglects the coupling between chemical order and size effects this model depends on three parameters:

- i) its number density ρ_m which is introduced into equation (7) to take into account the difference between model and experimental densities.

- ii) some diameter d_m whose value lies between d_1 and $\bar{d}$

- iii) and the first neighbour order parameter:

$$\xi = 1 - \frac{\eta_{12}}{\eta} \frac{1}{c_2} = 1 - \frac{\eta_{21}}{\eta} \frac{1}{c_1} \quad (9)$$

where η is the total coordination number and η_{12} the number of 2 atoms surrounding a 1 atom. Numerical values of these fit parameters are reported on table I.

The negative value of ξ expresses a chemical ordering phenomenon which is due to a preferential attraction between nickel and vanadium atoms and is responsible for the appearance of the

$\chi(Q)$ prepeak*. It should be interesting to compare these values with thermodynamical predictions but this is unfortunately impossible because the enthalpy of mixing of liquid Ni-V alloys has not yet been measured.

Although such an ordering phenomenon between two metals belonging to the beginning and to the end of the 3d transition series may look surprising it has also been observed by Sakata et al [16] in amorphous Cu-Ti alloys whose electronic structure is similar. In both systems, structural studies have thus opened the track to difficult thermodynamical or electronic properties measurements.

REFERENCES

- [1] J.L. LEMARCHAND, Thèse Ingénieur Docteur, INP GRENOBLE (1978).
- [2] J. BLETRY, Z. Naturforsch. a, 33, 327 (1978).
- [3] N.W. ASHCROFT, D.C. LANGRETH, Phys. Rev. 156, 685 (1966).
- [4] M. ALLIBERT, C. CHATILLON, R. MORACCHIOLI, A. PATTORET, C. SENILLOU, Brochure 66ème exposition de physique CNRS (1976) available at: LTPCM, ENSEEG, BP44 Domaine Universitaire 38401 St Martin d'Hères (France).
- [5] J. BLETRY, Thèse d'Etat, Grenoble (1979).
- [6] H.H. PAALMAN, C.J. PINGS, J. of Appl. Phys. 33, 2635 (1962).
- [7] I.A. BLECH, B.L. AVERBACH, Phys. Rev. 137, A 1113 (1965).
- [8] J.L. YARNELL, M.J. KATZ, R.G. WENZEL, S.M. KOENIG, Phys. Rev. A, 7, 2130 (1973).
- [9] L.S. ORNSTEIN, F. ZERNIKE, Proc. Acad. Sci. Amsterdam 17, 793 (1914).
- [10] O. HALPERN, M.H. JOHNSON, Phys. Rev. 55, 898 (1939).
- [11] M. WEBER, Thesis, Stuttgart (1978).
- [12] L.S. ORNSTEIN, F. ZERNIKE, Physik. Z. 19, 234 (1918).
- [13] G. TOURAND, Thèse d'Etat, Paris (1971).
- [14] Y. WASEDA, S. TAMAKI, Phil. Mag. 32, 273 (1975).
- [15] J. BLETRY, Z. Naturforsch. a, 32, 445 (1977).
- [16] M. SAKATA, N. COWLAM, H.A. DAVIES, J. Phys. F, 9, L 235 (1979).

* Such a prepeak cannot be explained by the presence of oxygen impurities since even if the 1000 ppm oxygen atoms were (very unlikely) only surrounded by nickel atoms (maximum order), that could only affect $10^{-3} \times 10$ (first neighbours) = 1 at % in nickel.