NEUTRON SMALL ANGLE SCATTERING FROM THE ALLOY Al-Zn ABOVE THE CRITICAL POINT

D. Schwahn, W. Schmatz

To cite this version:
D. Schwahn, W. Schmatz. NEUTRON SMALL ANGLE SCATTERING FROM THE ALLOY Al-Zn ABOVE THE CRITICAL POINT. Journal de Physique Colloques, 1977, 38 (C7), pp.C7-411-C7-413. <10.1051/jphyscol:1977783>. <jpa-00217286>

HAL Id: jpa-00217286
https://hal.archives-ouvertes.fr/jpa-00217286
Submitted on 1 Jan 1977

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.
NEUTRON SMALL ANGLE SCATTERING FROM THE ALLOY Al-Zn
ABOVE THE CRITICAL POINT (*)

D. SCHWAHN and W. SCHMATZ
Institut für Festkörperforschung der Kernforschungsanlage Jülich
5170 Jülich, Postfach 1913, Germany

Résumé. — La fluctuation cohérente de composition d’un alliage Al-Zn a été mesurée par diffusion aux petits angles des neutrons, dans un domaine de température de 435 °C et 324 °C. Aucune diffusion critique n’a pu être détectée au point critique incohérent. L’intensité des neutrons diffusés augmente continûment lorsque la température décroit de 435 °C à 324 °C. Au-dessous de \( T = 324 °C \) les courbes de diffusion diffèrent essentiellement des autres par leur grande intensité à petit \( k \) et leur décroissance rapide aux grandes valeurs de \( k \). Les résultats sont en accord avec la théorie de Cahn qui prédit une diminution du point critique réel à cause de la formation d’énergie élastique par la fluctuation de composition. La forte augmentation d’intensité au-dessous de \( T = 324 °C \) est due au comportement de décomposition rapide dans l’état instable du système.

Nous avons trouvé un déplacement d’environ \( \Delta T = 28 \) degrés en bon accord avec une évaluation théorique \( \Delta T = 25 \) degrés.

Abstract. — The coherent composition fluctuation in the system Al-Zn was measured by neutron small angle scattering in the temperature range between 435 and 324 °C. No critical scattering could be detected at the incoherent critical point. The intensity of the scattered neutrons increases continuously by decreasing the temperature from 435 to 324 °C. The scattering curves below \( T = 324 °C \) differ from the others essentially by their high intensity for small \( k \) and their strong decrease to larger \( k \) values. These results agree with Cahn’s theory which predicts a decrease of the real critical point due to the elastic energy built up by composition fluctuation. The strong increase of intensity below \( T = 324 °C \) is due to the rapid decomposition behaviour in the unstable state of the system. A shift of about \( \Delta T = 28 \) degrees was found which is in good agreement to a theoretical estimate of \( \Delta T = 25 \) degrees.

Introduction. — We measured \( \langle |c(k)|^2 \rangle \) i.e. the absolute square of the coherent composition fluctuation \( c(k) \) of a binary alloy above the critical point as a function of temperature by neutron small angle scattering. We chose the system Al-Zn with the critical composition \( c_{Zn} = 0.395 \) (figure 1). We intended to demonstrate experimentally:

1) Whether or not elastic energy \( \varphi_{el} \) due to the size difference of the components influences the stability of the system against decomposition. Following Cahn (1961) the additional elastic energy lowers the spinodal phase boundary (inside the spinodal is the unstable region). By this the metastable region becomes continuous from the low to the high composition side and therefore the critical point touches no more the stable region. An estimate gives a temperature shift of about 25 degrees for the critical point.

2) The singular behaviour of the composition fluctuation in the neighbourhood of the critical point.

(*) These results will be published in greater detail in Acta Met.

Scattering Law. — In a neutron small angle scattering experiment we measure the diffuse scattering cross
section $\frac{d\sigma}{d\Omega}(\kappa)$ which is proportional to $\langle |c(\kappa)|^2 \rangle$ (Krivoglaz, 1969).

$$\frac{d\sigma}{d\Omega}(\kappa) \propto \langle |c(\kappa)|^2 \rangle$$

(1)

$\langle |c(\kappa)|^2 \rangle$ can be expressed for small $\kappa$-values by thermodynamic functions as follows (Krivoglaz, 1969):

$$\langle |c(\kappa)|^2 \rangle = \frac{kT}{V} \left[ \frac{\partial^2}{\partial c^2} (g + \varphi_{\kappa}) + 2Bk^2 \right]$$

(2)

$B$ is the gradient energy coefficient. The term containing $B$ is due to the surface energy. $\frac{\partial^2}{\partial c^2} (g + \varphi_{\kappa})$ the second derivative of the Gibbs potential $(g + \varphi_{\kappa})$ with respect to the composition $c$, determines the stability of the system as defined by Gibbs. $g$ is the Gibbs potential per unit volume of the unstressed system. $\frac{\partial^2}{\partial c^2} (g + \varphi_{\kappa})$ is positive in the stable region of the phase diagram. It becomes zero at the spinodal and negative in the unstable region. Therefore $\langle |c(\kappa)|^2 \rangle$ and $\frac{d\sigma}{d\Omega}(\kappa)$ increases by lowering the temperature and become infinite for $\kappa = 0$ at the critical point which is a point of the spinodal.

Results. — Indeed, as shown in figure 2 and as predicted by eq. (2) the scattered intensity grows continuously as the temperature is lowered from 400 to 324 °C. The two curves measured below 324 °C differ from the others by their shape. Their intensity is much higher for small $\kappa$-values and their decrease to greater $\kappa$-values is much more pronounced. The behaviour of these curves is due to the decomposition of the system in the unstable state. As one can see the value of the critical temperature is about 324 °C. This is a shift of about 28 degrees due to elastic energy.

It should be mentioned that the curves measured in the metastable region are not so accurate as those measured in the stable region. In the metastable state beside the built-up of concentration fluctuations the system decomposes by nucleation and growth mechanism and therefore it is difficult to measure the coherent composition fluctuations. Thus, these curves were measured during the incubation time, when the decomposition mechanism is not yet of great influence. (A detailed description is given by D. Schwahn, 1977.)

Fig. 2. — Summary of the measurements of the coherent composition fluctuation. The change of the shape of the curves below 324 °C is due to the decomposition behaviour of the system in the unstable region.

Fig. 3. — $\frac{d\sigma}{d\Omega}(0)$ and $\kappa_m^2$ between 324 °C and 435 °C reflect the result of this experiment. At about 324 °C $\frac{d\sigma}{d\Omega}(0)$ becomes infinite and $\kappa_m^2$ zero which is due to the behaviour of the system at the critical point. The critical behaviour of both curves is classical. The full line curves are calculated independently from the neutron data. $\kappa_m^2$ depends sensitively on the range of the interaction potential as can be seen from the different slopes of the straight lines which are calculated from nearest neighbour interaction- and Lennard-Jones (6-12) potential (Cahn and Hilliard, 1958). The experimental values for the interaction potential range is in between the two theoretical ones.
Discussion. — To discuss the results we write the scattering law in a different form

\[
\frac{d\sigma}{d\Omega}(\mathbf{K}) = \frac{d\sigma}{d\Omega}(0) \frac{K_m^2}{K_m^2 + K^2}
\]

(3)

with

\[
\frac{d\sigma}{d\Omega}(0) \propto \frac{kT}{\frac{\partial^2}{\partial c^2} (g + \phi_e)}
\]

the cross section in forward direction and

\[
K_m^2 = \frac{\beta^2 (g + \phi_e)}{2B}
\]

the reciprocal square of the correlation length.

As can be seen from (3) \(\frac{d\sigma}{d\Omega}(0)\) and \(K_m^2\) completely describe the scattering law. They are plotted as a function of temperature in figure 3.

1) It can be concluded that the elastic energy produces the expected behaviour. \(\frac{d\sigma}{d\Omega}(0)\) becomes singular and \(K_m^2\) becomes zero at about 324 °C and not at 351.5 °C, which is the highest point of the two phase boundary. This point would be the critical point if the elastic energy \(\phi_e\) is zero. The difference of 27.5 degrees is in good agreement to theoretical calculations with the result of 25 degrees.

2) The critical behaviour of both parameters is classical. \(\frac{d\sigma}{d\Omega}(0)\) which is proportional to the susceptibility has a critical exponent of \(\gamma = 0.95 \pm 0.12\). The correlation length \(\xi = 1/K_m\) has a critical exponent of \(\nu = 0.5 \pm 0.03\). Near \(T_c\) this behaviour can only be understood if long range interaction energies are acting. This interaction is obviously caused by elastic energy. Finally, it should be mentioned that the full line curves in figure 3 are calculated without any relation to the neutron data. There is a reasonable agreement between these curves and the measured values.

References