Evaluation of diffuse neutron scattering at elevated temperatures and local decomposition in Ni-Au

M. J. Portmann, B. Schönfeld, and G. Kostorz

ETH Zürich, Institute of Applied Physics, CH-8093 Zürich, Switzerland

F. Altorfer

Laboratory for Neutron Scattering, ETH Zürich and Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland

J. Kohlbrecher

Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland

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It is demonstrated that in the diffuse neutron scattering of alloys at elevated temperatures (i) the temperature dependence of the linear absorption coefficient is the reason for problems encountered hitherto in the evaluation of diffuse wide-angle scattering and (ii) small-angle neutron scattering has to be corrected for thermal diffuse scattering. These corrections are applied to published data of Ni-8.4 at. % Au and Ni-9.6 at. % Ti and are used to firmly establish that local decomposition is also present in Au-rich Ni-Au above the miscibility gap.

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I. INTRODUCTION

Diffuse wide-angle scattering with neutrons and x-rays has proved to be a successful tool to determine the microstructure of solid solutions of alloys (for reviews, see, e.g., Refs. 1,2). For locally decomposed alloys, also small-angle scattering has to be measured to yield reliable data.

As an indicator of possible deficiencies in the evaluation (e.g., the values of the input parameters, the separation of the elastic- and inelastic-scattering contributions, the separation of short-range order and displacement scattering), the value of the Warren-Cowley short-range order parameter α_{000} is considered. By theory, α_{000} has to be one. While this requirement has often been fulfilled in diffuse scattering at room temperature and diffuse x-ray scattering at elevated temperatures, deviations were consistently reported for diffuse neutron scattering at elevated temperatures. For α_{000} , values much lower than one were obtained for Ni-V and Ni-Cr by Caudron *et al.*,³ for Pt-V and Ni-V by Le Bolloc'h,⁴ for Ni-Ti by Bucher *et al.*,⁵ and for Ni-Au by Portmann *et al.*⁶ Procedures for obtaining $\alpha_{000}=1$ varied between scaling the scattering intensity by a constant factor and adding a constant term to the scattering intensity, without giving a convincing explanation. As effective pair interaction parameters are based on the short-range order scattering, quite erroneous values might then result for the ordering energy (and thus on possible ground-state structures or the value of an order-disorder transition temperature).

In this investigation, the physical reason for the deficiencies mentioned above is addressed and an improved evaluation is applied to ⁵⁸Ni-8.4 at. % Au at 1083 K and ⁵⁸Ni-9.6 at. % Ti at 1103 K, two alloys previously investigated by the authors.^{5,6}

While local decomposition had been observed in Ni-8.4 at. % Au at 1083 K,⁶ local order was claimed to be present in Ni-60 at. % Au at 1023 K, on the basis of diffuse x-ray scattering.⁷ Local order was also expected from *ab initio* electronic structure calculations (see Ref. 8 and references therein), and Ni-Au was considered a rare example where the

high-temperature microstructure shows no remnants of the lower-temperature microstructure. A verification seemed indicated, especially as no small-angle scattering experiments had been performed. They were now done with thermal neutrons employing Ni-rich and Au-rich ⁵⁸Ni-Au alloys. Additionally, wide-angle scattering of Ni-60 at. % Au was measured to yield a comparison with the previous data from diffuse x-ray scattering.

II. EXPERIMENTAL

A Ni-60 at. % Au single crystal was grown by the Bridgman technique using isotopically pure (99.86 at. %) ⁵⁸Ni (State Scientific Center, Moscow, Russia) and 99.999+ % gold (Métaux Précieux SA METALOR, Neuchâtel, Switzerland). The sample used for wide-angle scattering was 2 mm in diameter and 10 mm in height. The measurement was performed at the triple-axis spectrometer RITA-II (PSI, Villigen, Switzerland) using a high-temperature furnace⁹ and an Eulerian cradle. Neutrons with an energy E of 14.68(50) meV were employed, together with a pyrolytic graphite filter to suppress λ/n harmonics. Data were exclusively taken along $h00$.

The polycrystalline plates used for small-angle neutron scattering (SANS) were 10 mm in diameter, and 2.7 mm in thickness for ⁵⁸Ni-8.3 at. % Au and 0.5 mm for ⁵⁸Ni-60 at. % Au. The grain size after plastic deformation and recrystallization, at 873 K, was smaller than 50 μm . Prior to the investigations, the samples were annealed at 1173 K for 5 days and quenched in brine. SANS patterns were taken on SANS-I (PSI, Villigen, Switzerland) equipped with a high-temperature furnace.¹⁰ Neutrons of a wavelength of 8.0(8) Å were employed. With a sample-to-detector distance of 2 m and a collimation length of 4.5 m, the magnitude of the scattering vector ($Q = 4\pi \sin \theta / \lambda$ where θ is half the scattering angle and λ the wavelength of the radiation used) covered by the two-dimensional position sensitive detector, was 0.02 to 0.24 Å⁻¹.

The small-angle and wide-angle scattering data were cali-

FIG. 1. Transmission factors of ^{58}Ni -8.4 at. % Au ($\circ$) and ^{58}Ni -9.6 at. % Ti ($\bullet$). The solid lines were calculated using the total thermal diffuse scattering cross section according to Kothari and Singwi¹¹ and scaled to the experimental transmission factors.

brated using the incoherent scattering of vanadium and measuring the background with an empty sample holder and with the sample replaced by Cd or boron nitride to block the direct beam.

III. DIFFUSE SCATTERING OF ^{58}Ni -8.4 AT. % Au AND ^{58}Ni -9.6 AT. % Ti

To obtain the temperature dependence of the linear absorption coefficient μ , the transmission factor was measured at RITA-II, using the same sample and the same setup as for diffuse wide-angle scattering, besides a 40' horizontal collimation and close defining slits in front of the sample. A steady decrease in the transmission factor is noted with increasing temperature for ^{58}Ni -8.4 at. % Au and for ^{58}Ni -9.6 at. % Ti (Fig. 1). For comparison, this factor was also calculated using

$$\mu = \frac{4}{a^3} (\sigma_{\text{coh}} + \sigma_{\text{inc}} + \sigma_{\text{abs}} + \sigma_{\text{TDS}}), \quad (1)$$

where a is the lattice parameter, σ_{coh} the total monotonic Laue scattering (if no Bragg reflection is excited), σ_{inc} the total incoherent scattering cross section, σ_{abs} the absorption cross section (calculated from tabulated values¹² for 1.798 Å), and σ_{TDS} the total thermal diffuse scattering cross section approximately given by Kothari and Singwi [Eq. (5.1) in Ref. 11] for coherent and incoherent one-phonon scattering. The values obtained for μ from the transmission factor were 1.60 cm^{-1} (1.95 cm^{-1}) for ^{58}Ni -8.4 at. % Au at 1083 K and 1.24 cm^{-1} (1.31 cm^{-1}) for ^{58}Ni -9.6 at. % Ti at 1103 K (the values in brackets were calculated using the scattering lengths and scattering cross sections as given by Sears¹²). For Ni-Ti, an uncertainty of $\pm 5\%$ in μ is estimated, arising from the cylindrical sample shape and the finite slit size, and somewhat larger for Ni-Au as the sample was thinner. The corresponding values previously used were calculated for 0 K (0.86 cm^{-1} in Ref. 5 and 1.41 cm^{-1} in Ref. 6). With the modified calculated values of μ and the resulting changes in multiple scattering, the original scattering data were reevaluated.

The new sets of the Warren-Cowley short-range order parameters α_{lmn} (l, m, n is the shell index in units of $a/2$) are

TABLE I. Sets of published Warren-Cowley short-range order parameters α_{lmn} for Ni-8.4 at. % Au and Ni-9.6 at. % Ti, together with those of the present reevaluation.

lmn	α_{lmn}			
	^{58}Ni -8.4 at. % Au		^{58}Ni -9.6 at. % Ti	
	Ref. 6	This work	Ref. 5	This work
000	0.594(29)	1.153(47)	0.5947(49)	0.8840(65)
110	0.133(11)	0.220(16)	-0.0608(12)	-0.0856(16)
200	0.084(10)	0.135(18)	0.0825(16)	0.1156(22)
211	0.015(6)	0.016(9)	-0.0075(9)	-0.0101(13)
220	0.008(4)	0.001(6)	0.0294(11)	0.0393(14)
310	0.021(4)	0.019(6)	-0.0111(8)	-0.0153(10)
222	-0.007(4)	-0.013(6)	0.0152(7)	0.0204(9)
321	0.000(2)	-0.002(4)	-0.0048(4)	-0.0065(5)
400	0.013(4)	0.022(7)	0.0127(8)	0.0173(10)
330	-0.001(3)	-0.001(5)	0.0009(5)	0.0013(7)
411	0.009(2)	0.017(4)	-0.0002(4)	0.0002(6)
420	0.006(2)	0.010(3)	0.0075(4)	0.0105(5)
233	-0.004(2)	-0.006(4)	-0.0015(4)	-0.0019(5)
422		-0.001(3)	0.0042(4)	0.0059(5)
431		-0.002(2)	-0.0018(3)	-0.0027(4)
510		0.014(4)	-0.0025(4)	-0.0037(5)
521		0.006(2)	-0.0013(3)	-0.0016(4)
440			0.0015(5)	0.0016(6)
433			-0.0008(3)	-0.0012(5)
530			0.0004(4)	0.0007(5)
244			0.0023(4)	0.0034(5)
600			0.0031(7)	0.0043(9)
532			-0.0002(3)	-0.0005(3)
611			-0.0007(4)	-0.0010(5)
620			0.0025(4)	0.0036(5)
541			-0.0004(3)	-0.0004(4)
622			0.0019(3)	0.0026(4)
631			-0.0010(3)	-0.0012(4)
444			0.0025(6)	0.0029(8)
543			-0.0006(2)	-0.0009(3)
550			-0.0002(5)	-0.0004(6)

given in Table I; the previously published parameter sets are added for comparison. It is noted that the values of α_{000} are now scattered around 1 and no longer systematically too low. The tentative correction for ^{58}Ni -8.4 at. % Au, applied by Portmann *et al.*⁶ (where half of the deviation of α_{000} from 1 was compensated by an additive term, the other half by a multiplicative factor), yields similar results for $\alpha_{lmn \neq 000}$ besides lower values for α_{110} and α_{200} . For ^{58}Ni -9.6 at. % Ti, no correction had been applied by Bucher *et al.*,⁵ i.e., an additive term had been tacitly evoked for the discrepancy. This now turns out to be inadequate. Thus, all $\alpha_{lmn \neq 000}$ are affected by the correction, and it must be concluded that the effective pair interaction parameters show a compositional dependence in Ni-rich Ni-Ti.

A correction of α_{000} is possible for other measurements if the dimensions of the samples were published, as this information is required to perform the corrections for absorption and multiple scattering. This was done for the samples inves-

FIG. 2. Small-angle scattering I_{SANS} (in Laue units, L.u.) of a ^{58}Ni -8.3 at. % Au polycrystal. Averaged values for scattering vectors between 0.08 and 0.24 $\text{\AA}^{-1}$ are shown for the as quenched state (from 1173 K) and states at elevated temperatures.

tigated by Caudron *et al.*³ While values of α_{000} , close to one, are now found for all measurements on Ni-33 at. % V (and remaining close to one with Pd-V), values much larger than one are found for the other alloys. As these measurements were all performed using alloys with natural Ni, they suffer from a large uncertainty of $\pm 0.6 b$ in σ_{inc} of natural Ni (amounting, e.g., to ± 0.5 in α_{000} with Ni-20 at. % Cr in Ref. 13). This underlines the advantage of using isotopes.

IV. LOCAL DECOMPOSITION IN Ni-Au

To support the results of local decomposition in Ni-8.4 at. % Au based on wide-angle scattering, the small-angle scattering of ^{58}Ni -8.3 at. % Au was measured (i) at 293 K for the as quenched state and (ii) between 993 and 1173 K within the solid solution. For all temperatures, a rapid increase in scattering intensity between 0.02 and 0.08 $\text{\AA}^{-1}$ is noted, which might occur because of large-scale fluctuations. From 0.08 to 0.24 $\text{\AA}^{-1}$ the scattering intensity is flat. The averaged values in this range decrease with decreasing temperature (Fig. 2). Attributing the temperature-dependent scattering to thermal diffuse scattering and approximating it by $\sigma_{\text{TDS}}/4\pi$ with σ_{TDS} as given by Kothari and Singwi,¹¹ the remaining elastic diffuse scattering amounts to 5.1 to 6.3 Laue units between 993 and 1173 K. These values are close to those measured for the as quenched state and agree with the extrapolated values from wide-angle scattering (see Fig. 3).

FIG. 3. Elastic diffuse scattering intensities I_{dif} (in Laue units, L.u.) of ^{58}Ni -60 at. % Au (circles) at 1023 K and ^{58}Ni -8.4 at. % Au (triangles) at 1083 K along $h00$ (h in reciprocal lattice units, r.l.u.). Open symbols: small-angle scattering, filled symbols: wide-angle scattering (up-triangles for $E = 14.68$ meV, down-triangles for $E = 4.76$ meV). The lines are to guide the eye.

Diffuse wide-angle scattering of ^{58}Ni -60 at. % Au was taken along $h00$ at 1023 K. There were about 200 to 700 counts per 90 min. In the evaluation, an overall (static and dynamic) Debye-Waller factor $\exp[-2B(\sin \theta/\lambda)^2]$ with $B = 2.37 \times 10^{-2} \text{ nm}^2$ was determined on the basis of estimated elastic constants $c_{11} = 181$ GPa, $c_{12} = 142$ GPa, and $c_{44} = 56$ GPa (Ref. 14). Data for both wavelengths smoothly overlap (Fig. 3). As in the case of ^{58}Ni -8.4 at. % Au, a strong minimum at the low-angle side of the 200 reflection is seen, reflecting the large linear displacement scattering. To decide whether there is a local maximum around 0.4 0 0 or not, small-angle scattering is required. Correcting the measured diffuse scattering for thermal diffuse scattering of ≈ 3.0 Laue units, a smooth overlap with the elastic diffuse wide-angle scattering is seen. Fig. 3 demonstrates that there is no maximum at 0.6 0 0, as claimed by Wu and Cohen,⁷ but at 000. The present small-angle and wide-angle scattering data support that Ni-60 at. % Au as well as Ni-8.4 at. % Au show local decomposition in the solid solution above the miscibility gap.

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