Direct Measurement of the Hydrogen-Hydrogen Correlations in Hydrogenated Amorphous $Ni_{56}Dy_{44}$ by Neutron Diffraction

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From an isotopic mixture of dysprosium with zero neutron scattering length and an isotopic mixture of nickel with zero neutron scattering length ribbons of the amorphous alloy $Ni_{56}Dy_{44}$ were produced by melt-spinning and loaded with 59 at% deuterium. A neutron diffraction experiment yielded directly the deuterium-deuterium partial structure factor S_{DD} and the partial pair correlation function G_{DD}. The incorporation of the D-atoms into the amorphous matrix shows an ordering up to five coordination shells at least. The main peak of G_{DD} is split up into a contribution at 2.36 Å with 5.4 nearest neighbours and a contribution at 2.76 Å with 4 neighbours. The D-atoms are located preferentially in Dy_4-tetrahedra, where the occupation of two neighbouring face-sharing tetrahedra is avoided.

1. Introduction

In previous studies [1 - 3] the structure of amorphous $Ni_{56}Dy_{44}$, loaded with 59 at% hydrogen, was investigated using X-ray- and neutron diffraction. The metal-metal and the metal-hydrogen correlations could be well characterized with the result that the hydrogen atoms occupy preferentially the centers of Dy_4-tetrahedra. For the hydrogen-hydrogen correlations only a shoulder at a H-H distance of 2.78 Å, sitting on a strong Dy-H peak, was discernible. In the present work the hydrogen-hydrogen correlations in amorphous $Ni_{56}Dy_{44}$ + 59 at% hydrogen were determined by neutron diffraction. In fact, the isotope deuterium was employed because of its much smaller incoherent scattering length and larger coherent scattering length. The principle of the procedure is to produce the amorphous alloy from zero-scattering isotopic mixtures of nickel (^{0}Ni) and of dysprosium (^{0}Dy), respectively, which is possible because for both elements a stable isotope with a negative neutron scattering length is available. A $^0Ni_{56}{}^0Dy_{44}$-alloy yields no coherent signal from nuclear scattering but only the incoherent and the paramagnetic scattering contributions which are treated as a background during the data reduction. After loading the $^0Ni_{56}{}^0Dy_{44}$-specimen with deuterium, a diffraction experiment will yield the coherent scattering from the deuterium atoms alone from which the deuterium-deuterium-correlations can be evaluated.

For the definitions and equations used in the present paper we refer to the review [4].

2. Experimental

2.1. Preparation of Amorphous $^0Ni_{56}{}^0Dy_{44}$ Ribbons

The zero-scattering mixture of nickel-isotopes, ^{0}Ni, was recycled from Ni-Dy-alloys already investigated previously [1 - 3]. Nickelhydroxide was isolated by wet chemistry and then oxidized. Finally, metallic nickel was obtained by reduction of the oxide under hydrogen. X-ray fluorescence analysis, electron beam microprobe analysis, and X-ray diffraction did not show any impurities. The ^{0}Dy material was produced by alloying the isotope ^{162}Dy (Fa. Chemotrade, Düsseldorf; Certification number 171541, isotopic enrichment 96.17 %) and a corresponding amount of natural Dy. From ^{0}Ni and ^{0}Dy the $^0Ni_{56}{}^0Dy_{44}$-alloy was prepared.

An amount of 3.6 grams of amorphous $^0Ni_{56}{}^0Dy_{44}$-ribbons was produced by melt-spinning under vacuum. X-ray diffraction proved that the ribbons were fully amorphous.

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2.2. *Loading the $^0Ni_{56}{}^0Dy_{44}$-specimen with Deuterium*

After the neutron diffraction run with the $^0Ni_{56}{}^0Dy_{44}$-sample it was loaded with 59 at% deuterium (purity 99.9 vol%) using a pressure hydrogen loading apparatus [1]. The absorption of deuterium by amorphous $Ni_{56}Dy_{44}$ took place only after grinding the surface of the specimen. Loading was carried out at a maximum D_2-pressure of 39.8 bar and a maximum temperature of 90 °C during 15 hours. The amount of deuterium absorbed by the sample was determined from the drop of the D_2-pressure in the loading cell. This yielded a deuterium content of 59 at %, i.e. the specimen finally had the composition $(^0Ni_{56}{}^0Dy_{44})_{41}D_{59}$. Additional analysis by means of gas-chromatography and the measurement of the weight of the sample before and after D-loading confirmed the value of the D-concentration, $c_D = 0.59 \pm 0.02$.

The densities were determined by the Archimedean method, which yielded for the atomic number densities of the blank sample and the D-loaded sample the values $\rho_0 = 0.0555$ Å^{-3} and $\rho_0 = 0.130$ Å^{-3}, respectively.

2.3. *Neutron Diffraction*

A neutron diffraction run with the $^0Ni_{56}{}^0Dy_{44}$-sample was done, which provided the magnetic and incoherent scattering contributions from the Ni- and Dy-atoms. After loading the sample with deuterium it was measured under the same conditions. The ribbons were filled into a cylindrical vanadium cuvette (outer diameter 11.7 mm, wall thickness 0.1 mm, height 45 mm). The diffraction experiments were performed with the 7C2 diffractometer at LLB, CE-Saclay, using the wavelength $\lambda = 0.70$ Å. The scattering data were recorded over the range of momentum transfer Q from 0.63 Å^{-1} up to 15 Å^{-1}. In addition to the measurement of the sample the following runs were done: Empty vessel, empty vanadium cuvette, vanadium rod, and cadmium rod. The corrections for counter efficiency and the absorption and background corrections according to [5] and conversion into absolute scattering units, employing the vanadium standard, finally yielded the differential cross section of the sample.

3. *Evaluation of the D-D Correlation Function*

3.1. *Separation of the Scattering Signal from the Deuterium Atoms*

Because of the zero scattering lengths of the Ni- and the Dy-atoms, two ways are possible to perform the data evaluation. One might treat the Ni-Dy-D system as a three-component one, where the atomic number density, $\rho_0 = 0.130$ Å^{-3}, includes all types of atoms, and evaluate the D-D correlation function as a partial function. Or one might treat the system as a single component system, consisting of D-atoms only, $\rho_{0,D} = c_D \cdot \rho_0 = 0.077$ Å^{-3}, and evaluate the D-D correlation function as a total function. In the following the second route is described, however we note that both routes yielded the same structural results.

Figure 1 presents the differential cross sections $d\sigma/d\Omega|_0(Q)$ (curve 1) and $d\sigma/d\Omega|_1(Q)$ (curve 2) for the blank sample and for the D-loaded sample, respectively, normalized to the number of D-atoms. $d\sigma/d\Omega|_0(Q)$ shows no structural features, but only the gradual decay due to the paramagnetic scattering of the Ni- and the Dy-atoms, which falls down to the constant level of the incoherent scattering in the range around $Q = 10$ Å^{-1}. $d\sigma/d\Omega|_1(Q)$ exhibits the oscillations due to the D-D correlations. The decay of this curve with increasing Q extends to larger Q-values than that for the blank sample, up to the maximum Q-value, which is due to the inelastic scattering effect from the D-atoms in addition to the magnetic

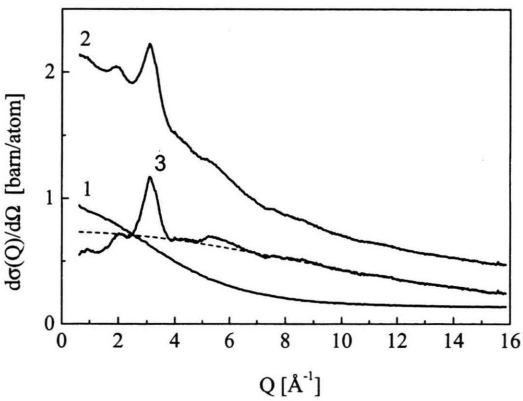

Fig. 1. Neutron scattering cross sections $d\sigma/d\Omega(Q)$ per D-atom. Curve 1: $^0Ni_{56}{}^0Dy_{44}$, curve 2: $(^0Ni_{56}{}^0Dy_{44})_{41}D_{59}$, curve 3: difference of curve 1 and curve 2, - - - $F_1(Q)$ according to (1), describing the inelastic effect by an exponential function.

scattering. The difference $d\sigma/d\Omega|_{D,1}(Q)$ of the two curves (curve 3) yields the scattering cross section (coherent plus incoherent) from the D-atoms alone. This approach, however, is based on the assumption that the magnetic scattering is not altered after loading the sample with deuterium. If this assumption does not hold strictly, as is to be expected, $d\sigma/d\Omega|_{D,1}(Q)$ will contain a remaining smoothly varying background (see below). The multiple scattering, estimated to be of the order of 4% of the total scattering [6], was assumed to cancel out in the difference function.

3.2. *Correction for the Inelastic Scattering Effect*

The difference function $d\sigma/d\Omega|_{D,1}(Q)$ in Fig. 1 still exhibits the inelastic scattering effect from the light D-atoms to be corrected for in the next step. As this correction can be done only in an empirical way, the conventional routes of extracting structure factors from neutron scattering cross sections, involving the analytical expression for the Placzek correction [7], cannot be followed. It is known that the inelastic scattering from hydrogen and deuterium atoms can be well described by an exponential decay in the range of large Q-values. Therefore $d\sigma/d\Omega|_{D,1}(Q)$ was fitted by the function

$$F_1(Q) = a \cdot \exp[-bQ^2] + c \qquad (1)$$

in the Q-range $Q > 7.8$ Å^{-1}, where a, b and c are the fitting parameters. In practice, this was done by subtracting a constant contribution c, which was chosen in

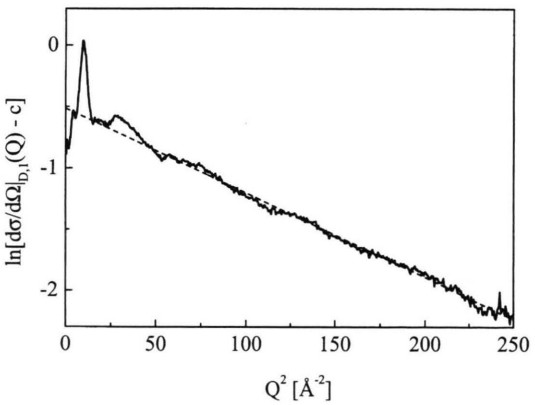

Fig. 2. Neutron scattering cross section of the D-atoms, $d\sigma/d\Omega|_{D,1}(Q)$, after subtraction of a constant contribution c. - - - $F_1(Q) - c$ according to (1).

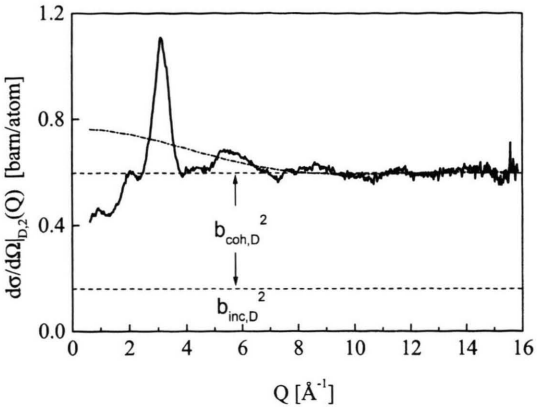

Fig. 3. Neutron scattering cross section of the D-atoms, $d\sigma/d\Omega|_{D,2}(Q)$, after correction for the inelastic effect according to (2). - · - $F_2(Q)$, describing a remaining inelastic effect.

such a way that the plot of $\log(d\sigma/d\Omega|_{D,1}(Q) - c)$ versus Q^2 in Fig. 2 follows a straight line (dashed line). The constant contribution c, whose physical origin is not specified, was subtracted, and the exponential $F_1(Q)$ was used as an empirical correction function for the inelastic effect according to

$$d\sigma/d\Omega|_{D,2}(Q) = \frac{d\sigma/d\Omega|_{D,1}(Q) - c}{(F_1(Q) - c)/a} + c. \qquad (2)$$

Figure 3 shows the corrected cross section $d\sigma/d\Omega|_{D,2}(Q)$. The level at large Q-values, 0.6 barn, agrees quite well with the sum of the squared coherent and incoherent scattering lengths of the D-atoms, $b_{coh,D}^2 + b_{inc,D}^2 = 0.607$ barn. However, towards smaller Q-values, say below 10 Å^{-1}, the curve still exhibits an increase, which indicates that the description of the inelastic scattering behaviour by an exponential function (1) does not hold at smaller Q-values. This feature has been observed already with hydrogen loaded amorphous Ti-Si and Al_2O_3 [8], and it requires a further correction step. The dot-dashed function $F_2(Q)$ in Fig. 3 was obtained by Fourier-filtering, which allows to separate long-wavelength variations from the structural oscillations, and was employed as a multiplicative term to correct $d\sigma/d\Omega|_{D,2}(Q)$.

3.3. *Evaluation of the Structure Factor and the Correlation Function*

The evaluation of the structure factor $S_{DD}(Q)$, according to

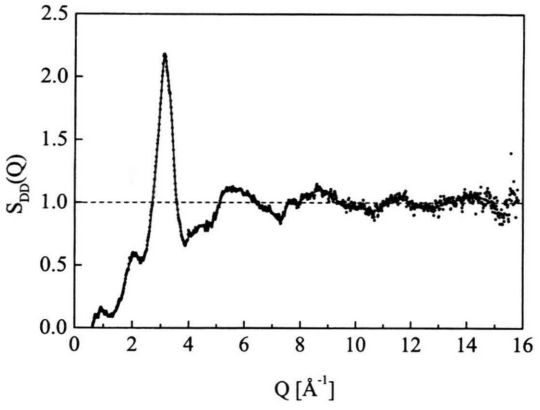

Fig. 4. Structure factor $S_{DD}(Q)$ according to (3). ··· experimental data, — spline fit.

$$S_{DD}(Q) = [d\sigma/d\Omega(Q) - b^2_{inc,D}]/b^2_{coh,D}, \quad (3)$$

involved the following steps: i) the correction with $F_2(Q)$, ii) renormalization, using the criterion that the Fourier-transform $G_{DD}(R)$ of $S_{DD}(Q)$ oscillates reasonably around the $-4\pi\rho_{0,D}R$ line at distances R below the first physical peaks, and iii) smoothing by a cubic spline fit. $S_{DD}(Q)$ is shown in Figure 4.

The reduced pair correlation function $G_{DD}(R)$, obtained by Fourier-transformation of $S_{DD}(Q)$,

$$G_{DD}(R) = \frac{2}{\pi}R\int Q^2[S_{DD}(Q) - 1]\frac{\sin QR}{QR}dQ \quad (4)$$

is plotted in Figure 5.

4. Discussion

The pair correlation function $G_{DD}(R)$ shows that the D-atoms in the amorphous $Ni_{56}Dy_{44}$-matrix are well ordered. We observe at least five coordination shells around a central D-atom at the distances (center of gravity) 2.56 Å, 4.48 Å, 6.4 Å, 8.4 Å, and around 10 Å. The first shell is splitted into two subshells at 2.36 Å and 2.76 Å, and the second shell is composed of three subshells. Also the higher coordination shells seem to be composed of subshells which, however, are blurred by the superimposed non-physical Fourier-ripples.

Figure 6 shows a fit to the first two maxima of the correlation function

$$g_{DD}(R) = 1 + G_{DD}(R)/4\pi R\rho_{0,D}, \quad (5)$$

Table 1. Comparison of amorphous $(Ni_{56}Dy_{44})_{41}D_{59}$ (a) and crystalline DyH_2 (c). R_{DD}: distance between D-atoms, Z_{DD}: coordination number. The numbering of shells refers to the amorphous alloy where (i) denotes a peak in the range between the first two shells.

No. of shell	1	(i)	2	3	4	5
(a) R_{DD}	2.36, 2.76	3.28	4.06, 4.48, 4.90	6.4	8.4	10
Z_{DD}	5.4, 4.0	3.8	5.6, 21, 12			
(c) R_{DD}	2.6	3.67	4.50			
Z_{DD}	6	12	8			

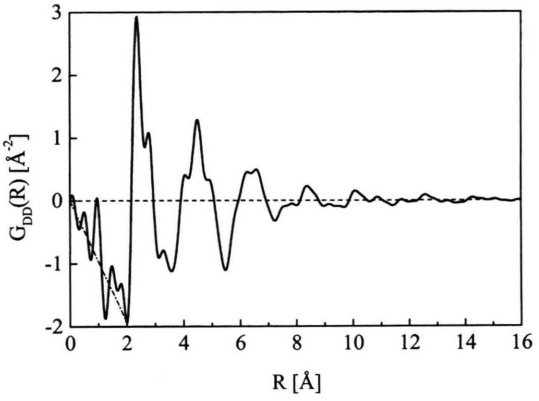

Fig. 5. Reduced pair correlation function $G_{DD}(R)$ according to (4). - - - $-4\pi\rho_{0,D} \cdot R$.

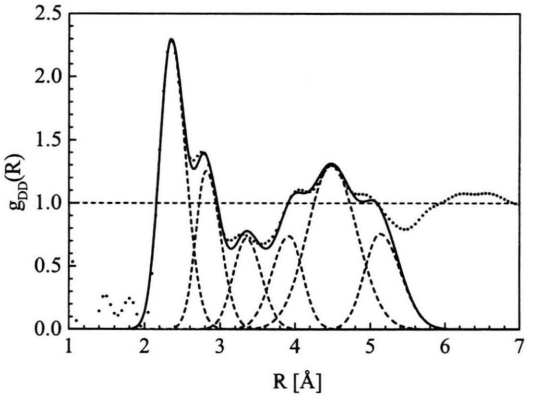

Fig. 6. Pair correlation function $g_{DD}(R)$. ··· experimental according to (5), — fit with Gaussians, - - - Gaussians for the individual peaks.

using for each subshell an asymmetric Gaussian. The structural parameters from the fit are listed in Table 1. The two Gaussians for the first coordination shell have the same width of about 0.4 Å and the same asymmetry with a half width of 0.17 Å at their left flank and 0.22 Å at their right flank. The corresponding coordi-

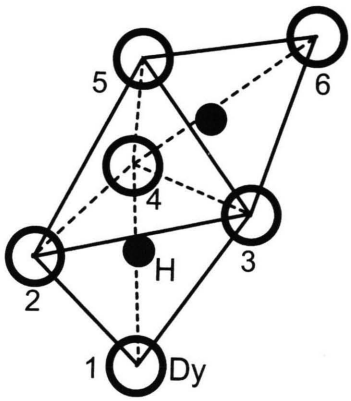

Fig. 7. Packing of three Dy_4-tetrahedra T_1 (1-2-3-4), T_2 (2-3-4-5) and T_3 (3-4-5-6). The face-sharing tetrahedra T_1 and T_2 do not accommodate a hydrogen atom at the same time. Nearest hydrogen neighbours are found in the edge-sharing tetrahedra T_1 and T_3.

nation numbers are $Z_{DD,I} = 5.4$ and $Z_{DD,II} = 4.0$, i. e. the D-atoms are surrounded by 9.4 D-neighbours on the average.

In the previous studies [1 - 3] on hydrogenated amorphous Ni-Dy alloys some structural similarities with the crystalline hydride DyH_2 have been found, such as a tetrahedral surrounding of the hydrogen atoms by Dy-atoms. In Table 1 the D-D distances and coordination numbers for amorphous $Ni_{56}Dy_{44}$ + 59 at% H and for the crystalline hydride DyH_2 are compared. In the cubic DyH_2 phase (cF12 structure) the hydrogen atoms occupy the tetrahedral sites in the fcc-matrix of the Dy-atoms. The mean value of the positions of the two subpeaks of the first shell for the amorphous alloy, 2.56 Å, agrees well with the distance $R_{DD} = 2.60$ Å in crystalline DyH_2, and also the distance around 4.5 Å is found in the glass as well as in the crystalline hydride. However, the distance $R_{DD} = 3.67$ Å in DyH_2 does not occur in the amorphous alloy, and the coordination numbers are different. This indicates that the packing of hydrogen-centered Dy_4-tetrahedra differs in the amorphous phase from that in the crystalline phase, which is not surprising because of the cubic symmetry of the DyH_2 phase.

The distance between the centers of two face-sharing Dy_4-tetrahedra, as sketched in Fig. 7, where $R_{DyDy} = 3.77$ Å [1 - 3], is 1.54 Å. Although the D-D correlation function in Fig. 5 is disturbed by the Fourier-ripples at small R-values, the existence of a substantial peak at this distance can be excluded, which means that the D-atoms do not occupy the nearest centers of tetrahedra. But the average D-D distance for the first shell, $R_{DD} = 2.56$ Å, agrees well with the distance, 2.51 Å, between the centers of two edge-sharing tetrahedra which have a tetrahedron between them (see Figure 7). Noting that around a central tetrahedron 6 positions for such edge-sharing tetrahedra are possible, the average coordination number $Z_{DD} = 9.4$ appears rather high. On the other hand, it is well known that the structures of real metallic glasses do not consist of a packing of ideal tetrahedra. Descriptions of the structure of metallic glasses in terms of tetrahedra require a high degree of distortions.

5. Conclusions

By neutron diffraction with an amorphous zero-scattering $Ni_{56}Dy_{44}$ alloy, containing 59 at% deuterium, the direct observation of the D-D correlation function was possible. The positional correlations between the deuterium atoms exhibit a high degree of order. The D-atoms avoid to occupy face-sharing Dy_4-tetrahedra, but are found in neighbouring tetrahedra which have a common edge and a tetrahedron in between. The first coordination shell of about nine D-neighbours is split up into two subshells with five and four neighbours.

Acknowledgements

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