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Local deuterium order in apparently disordered Laves phase deuteride $YFe_2D_{4.2}$

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ABSTRACT

Deuterium short-range order in cubic Laves phase deuteride $YFe_2D_{4.2}$ was studied by neutron (*ToF*) powder diffraction experiments and Pair Distribution Function (PDF) analysis between 290 and 400 K. The minimal allowed D–D distance of 2.1 Å in a metal deuteride (Switendick rule) has been experimentally proved in the HT-disordered phase $YFe_2D_{4.2}$. It has been found that the distribution of deuterium atoms around the iron is not random, and cannot be explained only by applying the Switendick rule. The first coordination sphere of iron atoms in the high temperature (HT)-disordered phase resembles between 350 and 400 K the coordination observed in the low temperature (LT)-ordered phase. Reversed Monte Carlo modeling of the Pair Distribution Function of the HT-disordered phase prefers the coordination FeD_5 and FeD_4 in agreement with the LT-ordered phase.

1. Introduction

The deuterides of cubic (C15) Laves phases AB_2 (A-rare earth, B-transition metal) have been widely studied for the influence of deuterium absorption on their magnetic properties. YFe_2, which can absorb up to 5H per formula unit (/f.u.), is particularly interesting owing to the large variety of crystal structures obtained at different hydrogen content [1–8]. These crystal structures are related to an ordering of hydrogen atoms on interstitial sites below an order–disorder temperature T_{OD}, which leads either to superstructures or to a distortion of the cubic C15 structure. The deuterium rich phase $YFe_2D_{4.2}$ shows complex magnetic and structural behavior and was object of numerous studies [7–10].

1.1. Structural models of HT-disordered and LT-ordered $YFe_2D_{4.2}$ phases

Above $T_{OD}=338$ K, $YFe_2D_{4.2}$ crystallizes in the cubic structure (Fd-$3m$, $a=7.95$ Å); between 332 and 338 K it shows a rhombohedral distortion (R-$3m$, $a=5.702$ Å, $c=12.404$ Å) [7]; and below 332 K it has a monoclinic superstructure (Pc, $a=5.5066$, $b=11.4823$, $c=9.4292$ Å, $\beta=122.33^\circ$ at 290 K) [9,10].

The LT-ordered monoclinic $YFe_2D_{4.2}$ contains seven of eight independent iron atoms coordinated by deuterium in a trigonal bipyramid. The eighth iron atom (Fe8) is coordinated by four deuterium in a tetrahedral configuration. Most D–D distances are, within the precision of the diffraction experiment, longer than 2.1 Å; the shortest ones are of 1.96 Å. Among 64 available sites (48 sites A_2B_2 and 16 sites AB_3) 18 sites (15 sites A_2B_2 and 3 sites AB_3) were occupied by deuterium, from which 10 sites not fully (occupancy between 0.835 and 0.974). The notation A_2B_2 and AB_3 of the deuterium sites refers to the tetrahedral coordination of the sites by the metals. The refined composition of the LT-ordered phase is therefore $YFe_2D_{4.27(5)}$ in agreement with the D content obtained by the volumetric method. See Ref. [10] for more details and for structural drawings.

The structural model of the HT-disordered cubic phase as seen by the Rietveld refinement is shown in Fig. 1. Deuterium atoms are distributed on two Wyckoff sites, 96g and 32e, with tetrahedral coordination by metals (A_2B_2 and AB_3, resp.) with a strong preference for the 96g site and third available tetrahedral site 8b (B_4) empty (see Supporting Information, Table S1, Fig. S1 and Ref. [10]). The total number of deuterium atoms in one cubic unit cell of the HT-disordered phase is 34 if calculated from the refined composition of the LT-ordered phase, and 37 as refined for the HT-disordered phase. This discrepancy was discussed in [10] in view of not exact treatment of the diffuse intensity in the neutron powder pattern of the HT-disordered phase by Rietveld refinement. In our next analysis of the HT-disordered phase we will introduce 34 deuterium atoms/cubic unit cell. Our choice to work with 34 instead of 37 atoms is based on the observation that the order–disorder transition between the LT- and HT-phases is fully reversible, and the Rietveld refinement of the ordered LT-phase is

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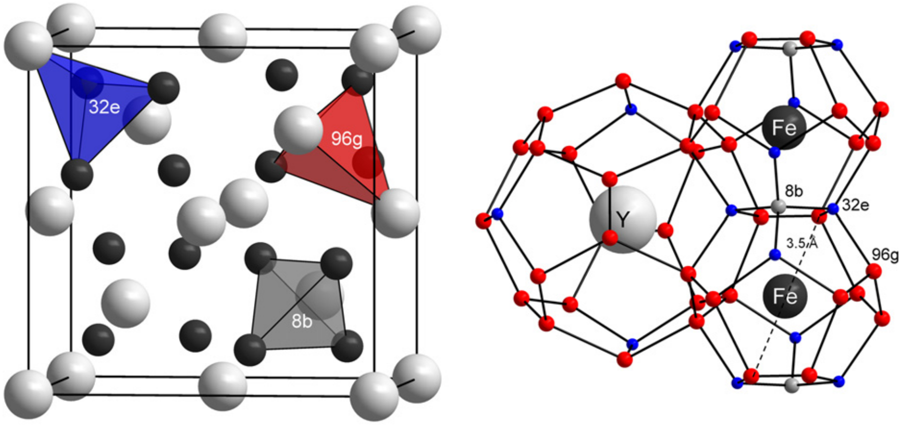

Fig. 1. Structural model of the HT-disordered phase as seen by the Rietveld refinement. Left: one cubic unit cell, yttrium as light and iron as dark spheres. Deuterium atoms are distributed on two Wyckoff sites, 96*g* and 32*e*, with tetrahedral coordination by metals (A_2B_2 and AB_3, respectively) with a strong preference for the 96*g* site and third available tetrahedral site 8*b* (B_4) empty. Right: coordination of yttrium and iron atoms by the deuterium. The maximal distance of 3.5 Å between two deuterium atoms in the first coordination sphere of the iron is shown by a dashed line.

more reliable as the powder pattern contains only Bragg contribution and no diffuse intensity.

The order–disorder transitions very often include a short-range order (SRO) in the disordered phase as a precursor to an ordering phase transition inducing the long-range order (LRO). A classic example is the ordering of deuterium atoms in deuterides of *bcc* metals like $VD_{0.8}$ [11] or $PdD_{0.5}$ [12]. The question whether the SRO exists also in the HT-$YFe_2D_{4.2}$ cannot be answered from the analysis of Bragg scattering, therefore the diffuse intensity in the neutron scattering data must be analyzed. Indeed the diffuse intensity was observed in the neutron powder patterns of HT-$YFe_2D_{4.2}$ [10]. The SRO of deuterium atoms in HT-disordered cubic Laves phases was observed and explained for HfV_2D_4 [13], ZrV_2D_4 [14] and for $ZrCr_2D_4$ [15]. It was found that the dominating contribution to the neutron diffuse scattering comes from the chemical SRO between deuterium atoms and vacancies on 96*g* and 32*e* Wyckoff sites. In $ZrCr_2D_4$ also the displacive SRO was modeled. No D–D distances shorter than 2.1 Å have been observed, strong D–D correlations up to 4 Å, and no D–D correlations (random D distribution) above 12 Å have been concluded from the Reversed Monte Carlo modeling in the reciprocal space.

In this paper we will show that the SRO also exists in the HT-$YFe_2D_{4.2}$, and we will compare it to the LRO as observed in the LT-$YFe_2D_{4.2}$. As the experimental method we will use the Pair Distribution Function analysis of the diffuse intensity in the neutron powder pattern.

2. Experimental

2.1. Sample synthesis and DSC measurement

The YFe_2 intermetallic compound was prepared by induction melting of the pure elements followed by 3 weeks of annealing at 1100 K. The composition and homogeneity was checked by X-ray powder diffraction (XPD) using a Bruker D8 diffractometer (Cu $K\alpha$ radiation) and electron probe microanalysis (EPMA) as described in [7]. The $YFe_2D_{4.2}$ deuteride was prepared by solid-gas reaction using a Sievert apparatus as described in [7], and its homogeneity was checked by XPD. The sample used for the PDF analysis in this paper corresponds to the sample no. 1 from the Ref. [10].

The thermal behavior of the order–disorder transition was measured using a differential scanning calorimeter DSC Q100 from TA instrument, with heating rate of 5 and 10 K/min.

2.2. Pair Distribution Function analysis

The analysis of the Bragg scattering assumes a LRO in the crystal, and is done for polycrystalline samples via Rietveld refinement [16]. Deviations from the LRO result in the occurrence of diffuse scattering which contains information about SRO of atoms. In a total scattering experiment which samples Bragg and diffuse scattering data simultaneously the information about SRO is preserved. There are various ways to extract information about the SRO from the analysis of single crystal diffuse scattering [17]. Significant, and often sufficient, information can be gleaned from the analysis of the atomic Pair Distribution Function (PDF) obtained from the total scattering from powder samples, and experiment as well as data analysis are in general less complicated. In fact the PDF method was originally applied to the study of liquids and amorphous materials [18], but can also be applied to disordered crystalline materials [19].

The PDF gives the volume normalized probability of finding an atom at a given distance r from another atom. In other words it can be understood as a bond length distribution of the material weighted by the respective scattering powers of the contributing atoms. The PDF can be calculated from a structural model, according to the definition of $\rho(r)$ from [20], by a relation

$$G_{calc}(r) = \frac{1}{r}\sum_{ij}\left[\frac{b_i b_j}{\langle b \rangle^2}\delta(r - r_{ij})\right] - 4\pi r \rho_0 \qquad (1)$$

where ρ_0 is the average number density. The sum goes over all pairs of atoms i and j within the model crystal separated by r_{ij} [19]. The scattering power of atom i is b_i and $<b>$ is the average scattering power of the sample. In the case of neutron scattering b_i is simply the scattering length of the atom i.

The observed PDF is obtained [21,22] from the powder diffraction data via a *sine* Fourier transform of the normalized total-scattering structure function $S(Q)$

$$G_{obs}(r) = 4\pi r[\rho(r) - \rho_0] = \frac{2}{\pi}\int_0^\infty Q[S(Q) - 1]\sin(Qr)dQ \qquad (2)$$

where $\rho(r)$ is the microscopic pair density.

2.3. Time-of-flight neutron data

The time-of-flight (*ToF*) neutron powder data were collected at the GPPD diffractometer at the IPNS, Argonne National Laboratory