Deuterium Interaction with fcc Iron at High Pressures and Temperatures

I.A. Sholin[1,2]*, V.E. Antonov[1], V.M. Gurev[1,2], V.I. Kulakov[1], M.A. Kuzovnikov[1,3] and V.Y. Zuykova[1,2]

[1] *Institute of Solid State Physics RAS, 142432 Chernogolovka, Moscow District, Russia*
[2] *Moscow State University, 119992 Moscow, Russia*
[3] *Max Planck Institute for Chemistry, 55128 Mainz, Germany*

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*e-mail: sholin@issp.ac.ru

At room and lower temperatures, hydrogen atoms occupy octahedral (O) interstitial sites in all known monohydrides of d-metals with close-packed metal lattices (fcc, hcp or double hcp) (see [1] and references therein). On the other hand, the ground-state energy of the H atom sitting on an alternative tetrahedral (T) interstitial site is not much higher. This opens the possibility of a partial Boltzmann occupancy of the T-sites at elevated temperatures.

A considerable T-occupancy reaching about 1/3 of all D atoms has for the first time been found in fcc deuterides of palladium by *in situ* neutron diffraction at 310 °C and deuterium pressures up to 9 MPa [2, 3]. A few years later, another *in situ* ND investigation showed that about 1/6 of D atoms are likely to occupy the T-sites in fcc deuteride of iron at T = 715 °C and P = 6.3 GPa [4].

The subtle difference between the profile fits using the O-model and O+T model was not however sufficient to establish the presence of D atoms on the T-sites with certainty. At the same time, modeling this pattern assuming that D atoms could fill only the O-sites and allowing them to occupy both O- and T-sites gave noticeably different total D/Fe ratios of 0.47 and 0.64, respectively [4].

In order to examine which of the two predicted D/Fe values better agrees with experiment, we constructed an isobar of deuterium solubility in iron at P = 6.3 GPa and temperatures from 100 to 800 °C using a quenching technique [5]. The point (6.3 GPa, 715 °C) chosen for the experiment in Ref. [4] and the temperature interval of the isobar constructed in the present work are shown on the T-P diagram of the Fe-H system (Fig. 1) copied from Ref. [6]. The isobar is presented in Fig. 2.

As one can see from Fig. 2, our experiment confirms the value of D/Fe = 0.64(3) resulting from the O+T model [4]. Such a value corresponds to the deuterium-induced volume expansion of fcc iron dV_a/dx = 2.21(4) Å^3/atom D [4], and therefore this estimate of Ref. [4] is also confirmed.

The isobar in Fig. 2 also demonstrates a step-wise decrease in the deuterium solubility in iron from D/Fe =1 to D/Fe ≈ 0.9 at T_0 ≈ 260 °C due to the transition from the low-temperature stoichiometric dhcp (ε′) FeD phase to the high-temperature fcc (γ) Fe-D phase with a variable composition. Since the direct synthesis of single-phase samples of ε′-FeD from α-Fe at a pressure of 6.3 GPa is not possible for kinetic reasons, the points shown by the solid blue triangles were obtained with the samples first transformed to γ-FeD_x at 500 °C.

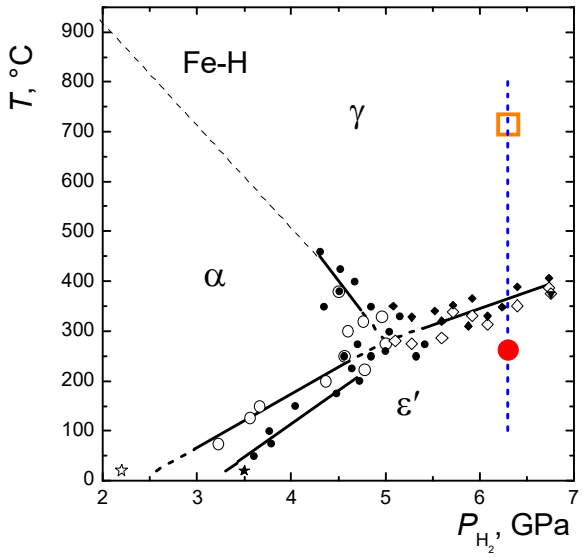

Figure 1. T-P diagram of the Fe-H system [4]. α – dilute H solutions in bcc Fe; γ – hydrogen solutions in fcc Fe with the H/Fe ratio varying from x = 0 to x ≈ 1 depending on the temperature and pressure; ε′ - a stoichiometrc hydride FeH with a double hcp metal lattice.

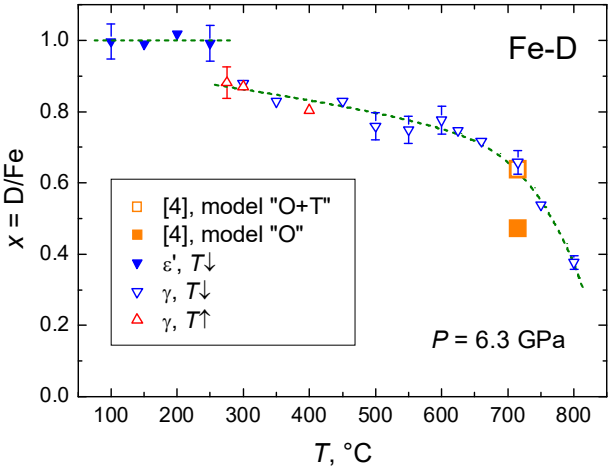

Figure 2. Isobar of equilibrium deuterium solubility in fcc Fe at a pressure of 6.3.GPa.

To determine the temperature hysteresis of the ε′↔γ transformation, 3 single-phase ε′-FeD samples formed at 6.3 GPa and 200 °C were further heated again and exposed for 1 day to a higher temperature (red open up-

triangles in Fig. 2). As one can see, the ε′↔γ transformation showed no hysteresis within the experimental accuracy of ±15 °C.

The obtained point of the ε′↔γ transformation in the Fe-D system is shown with a solid red circle in Fig. 1. It lies approximately 100 °C below the line of this transformation in the Fe-H system constructed earlier [4].

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