Supplementary material to the article “Synthesis and superconducting properties of some phases of iron polyhydrides at high pressures”

1. Determination of the volume per iron atom V_{Fe} at pressure increase and during phase transitions based on microphoto processing

1.1. Calculation of the specific volume of iron V_{Fe} based on microphoto processing data

During the study of Fe, FeH_x(I) and FeH_x(II) samples, careful measurements of Raman spectra were carried out at each value of the applied pressure, as well as photography and measurement of the area S from the sample images. The experimental dependence *S(P)* on pressure allows the dependence of the specific volume V_{Fe}(P) on pressure for all transformations to be constructed. If we assume that the compression conditions are hydrostatic and the sample is isotropic, then changes in the total volume of the sample depend on changes in its visible area can be expressed as:

$$V = S \cdot h = \alpha \cdot S \cdot S^{1/2} = \alpha \cdot S^{3/2}, \qquad (1.1)$$

where V - is the volume of the sample, S - is its area, h - is the thickness of the sample, $\alpha = h_0/S_0^{1/2}$ is a coefficient calculated from the initial values of the area (S_0) and thickness (h_0) of the sample at the initial pressure P_0. The number of iron atoms in the sample N_0 is calculated based on the known equation of state of the ε-Fe phase at volume V_0 and initial pressure P_0:

$$N_0 = V_0/V_{Fe}(P_0)\ , \qquad (1.2)$$

where $V_0 = S_0 \cdot h_0 = \alpha \cdot S_0^{3/2}$ – is the experimentally measured volume of the sample at initial pressure P_0, $V_{Fe}(P_0)$ – is the specific volume of the iron atom at pressure P_0 from the known equation of state of the ε-Fe phase. The value of N_0 remains constant throughout the experiment. As a result, calculations can be made for the pressure dependence of the specific volume of the iron atom in the sample:

$$V_{Fe}(P) = \frac{V(P)}{N_0} = \frac{\alpha \cdot S^{3/2}}{N_0} = \frac{\alpha \cdot S^{3/2}}{\alpha \cdot S_0^{3/2}} V_{Fe}(P_0) = \frac{S^{3/2}}{S_0^{3/2}} V_{Fe}(P_0) \qquad (1.3)$$

Finally we have:

$$V_{Fe}(P) = \frac{V_{Fe}(P_0)}{S_0^{3/2}} S(P)^{3/2} \qquad (1.4)$$

Thus, under the conditions of hydrostaticity, an isotropic sample and free boundaries, the dependence of the volume on the visible area obeys the law $V \sim S^{3/2}$.

1.2. Comparison of the volume of iron V_{Fe}, calculated from microphoto data, with experiment

The figure 1 shows the dependences of sample volumes calculated from micrographs using the ratios $V \sim S^1$ and $V \sim S^{3/2}$, in comparison with the results of the XRD experiment.

We found that the experimental volume dependence calculated from the visible area of the sample from the relation $V \sim S^{3/2}$ is in poor agreement with the experimental data obtained in XRD experiments. If we accept the relation $V \sim S^1$, then only in this case the data calculated from the visible area of the sample correspond very well to the results of the XRD experiment.

This dependence occurs in the case of constant sample thickness. This indicates that in our cell the compression conditions of the sample are such that its volume is mainly determined by the change in the area of the sample, while its thickness practically does not change, or changes much less than the area.

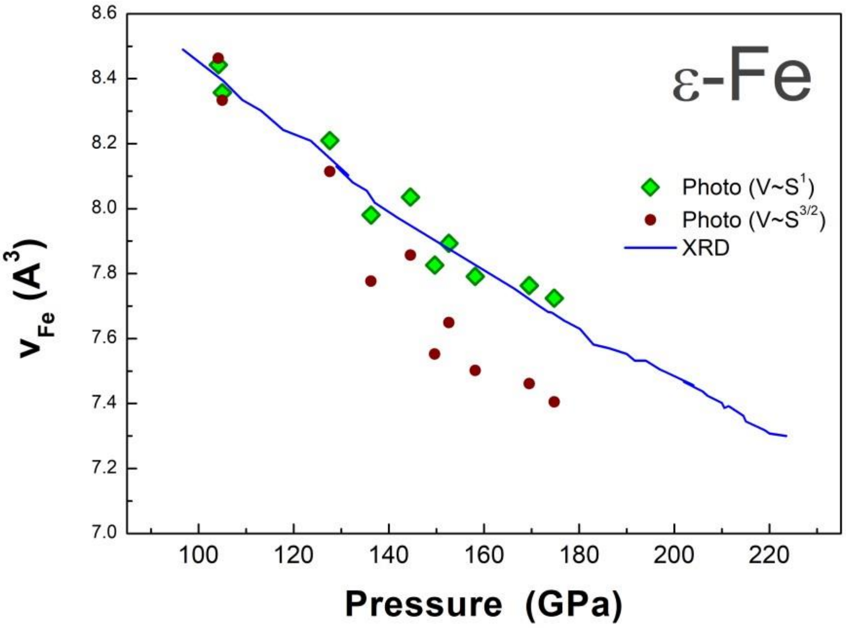


Figure 1. The dependence of the sample volume calculated from the relation $V \sim S^1$ is in good agreement with the results of the XRD experiment.

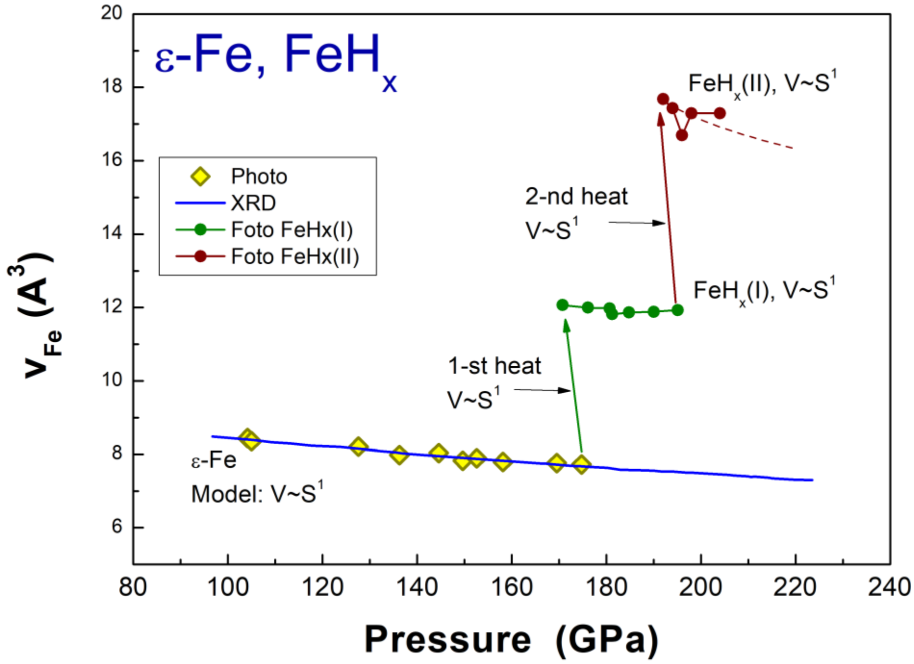


Figure 2. Pressure dependence of the specific volume of iron in polyhydrides FeH_x(I) and FeH_x(II) in the 1st model, when $V \sim S^1$ both with a change in pressure and with laser heating.

There are two reasonable models for calculating the volume during the synthesis of FeH_x:

(1) In the first model, both when the pressure changes and when the sample is synthesized during the heating process, the volume changes according to the relationship $V \sim S^1$ (i.e., the thickness of the sample remains constant, and the change in volume is due only to a change in the area of the sample).

(2) In the second model, when the pressure changes, the volume changes according to the law $V \sim S^1$, and when a sample is synthesized, the volume changes according to the relation $V \sim S^{3/2}$. In the

latter case, it is assumed that the high temperature during synthesis creates almost ideal hydrostatic conditions and the isotropic sample expands uniformly in all three dimensions.

The figure 2 shows the pressure dependence of the specific volume of iron in polyhydrides FeH_x(I) and FeH_x(II) within the 1st model, under the condition V ~ S1, both with a change in pressure and with laser heating.

The figure 3 shows the pressure dependence of the specific volume of iron in the polyhydrides FeH_x(I) and FeH_x(II) within the 2nd model. Here the relation $V \sim S^1$ with pressure changes and the relation $V \sim S^{3/2}$ with laser heating are satisfied.

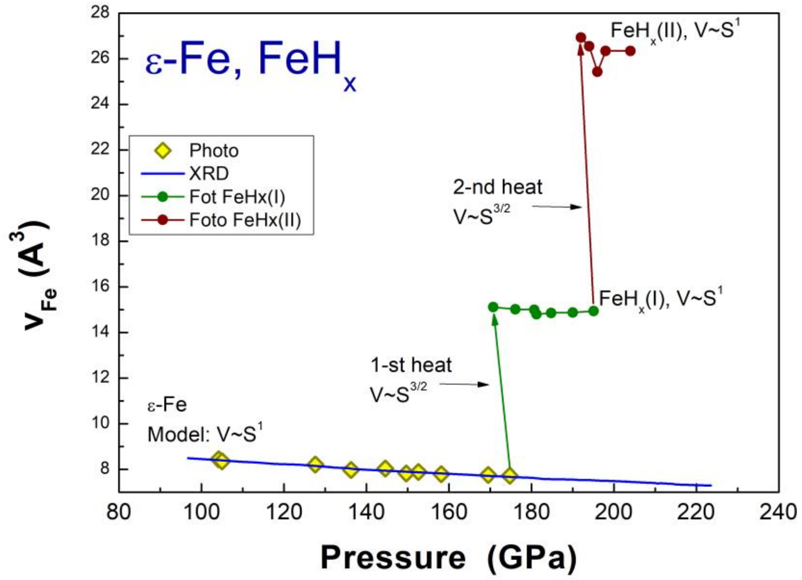


Figure 3. Pressure dependence of the specific volume of iron in FeH_x(I) and FeH_x(II) polyhydrides within the framework of the 2nd model, $V \sim S^1$ with a change in pressure, and $V \sim S^{3/2}$ with laser heating.

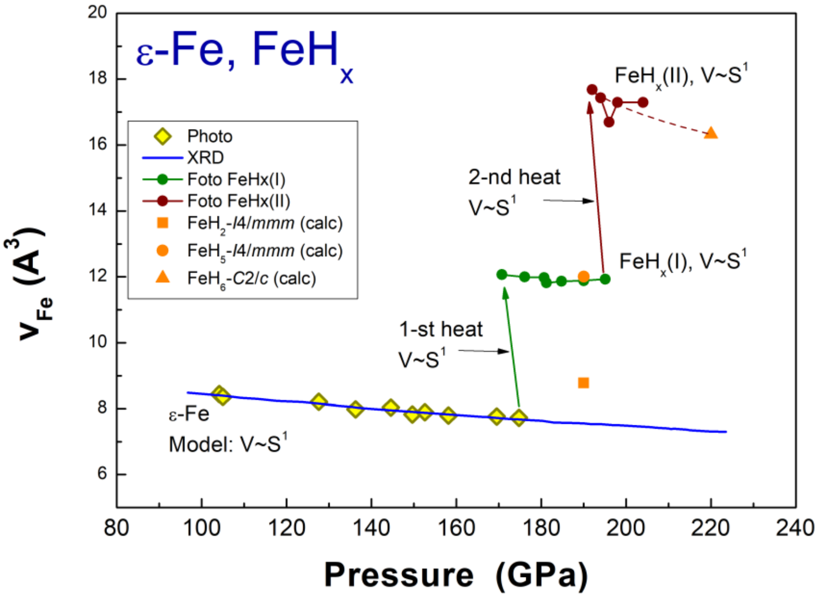


Figure 4. Pressure dependence of the specific volume of iron in polyhydrides FeH_x(I) and FeH_x(II) within the framework of the 1st model, when $V \sim S^1$ both with a change in pressure and with laser heating. Compared with theoretical calculations for the phases FeH_2, FeH_5 and FeH_6.

Comparison with theoretical calculations of the results of our measurements of the specific volume of the iron atom, obtained from the analysis of microphotographs of the sample, revealed a very good correlation of our data with the structure of the FeH_x(I) and FeH_x(II) phases within the framework of the 1st model, when the relation $V \sim S^1$, both with changes in pressure and with laser heating.

The comparison results are shown in figure 4.

Thus, it has been established that the volume of the sample changes proportionally to the visible area $V \sim S^1$, both with increasing pressure and with each subsequent synthesis as a result of laser heating. When compared with theoretical calculations, it turned out that the specific volume per iron atom in the FeH_x(I) phase corresponds to the FeH_5 phase, and in the FeH_x(II) phase corresponds to the FeH_6 structure (see Fig. 4).

2. Pressure determination from Raman spectra (evaluation of gradient and accuracy)

In our work, we used a pressure calibration scale based on the broadening of the first Raman peak from the diamond anvil. There are many works on the creation of this scale, but the most detailed and consistent information on this scale is presented in the work of Akahama [1]. Depending on the "rigidity" of the medium transmitting pressure, different versions of the diamond scale are used. Akahama proposed the following formula for determining pressure

$$P(GPa) = K_0 \frac{\Delta \nu}{\nu_0}\left[1 + \frac{1}{2}(K_0' - 1)\frac{\Delta \nu}{\nu_0}\right], \tag{2.1}$$

where $\nu_0 = 1334$ см$^{-1}$ – is the position of the first peak of Raman scattering for diamond, $\Delta\nu$ - is the broadening of this peak under the influence of pressure. The parameters K_0 и K_0' for strongly nonhydrostatic conditions are respectively equal to K_0 = 547(11) GPa and K_0' = 3.75(0.2). For conditions close to hydrostatic, the scale is significantly "softer": K_0 = 445(20) GPa and K_0' = 3.5(0.5), respectively. The figure 5 shows, as an example, the characteristic spectra of Raman scattering from a diamond anvil at different pressures in different media.

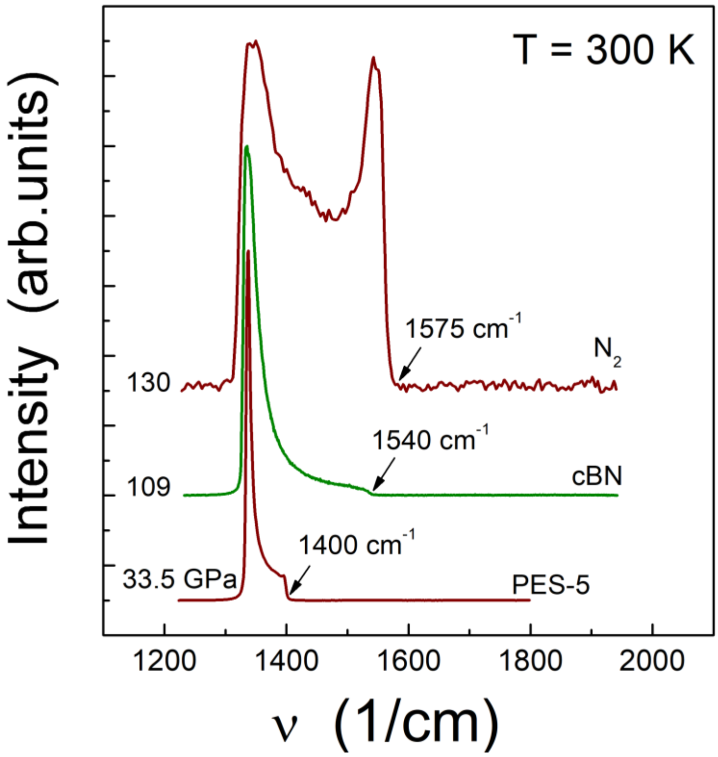
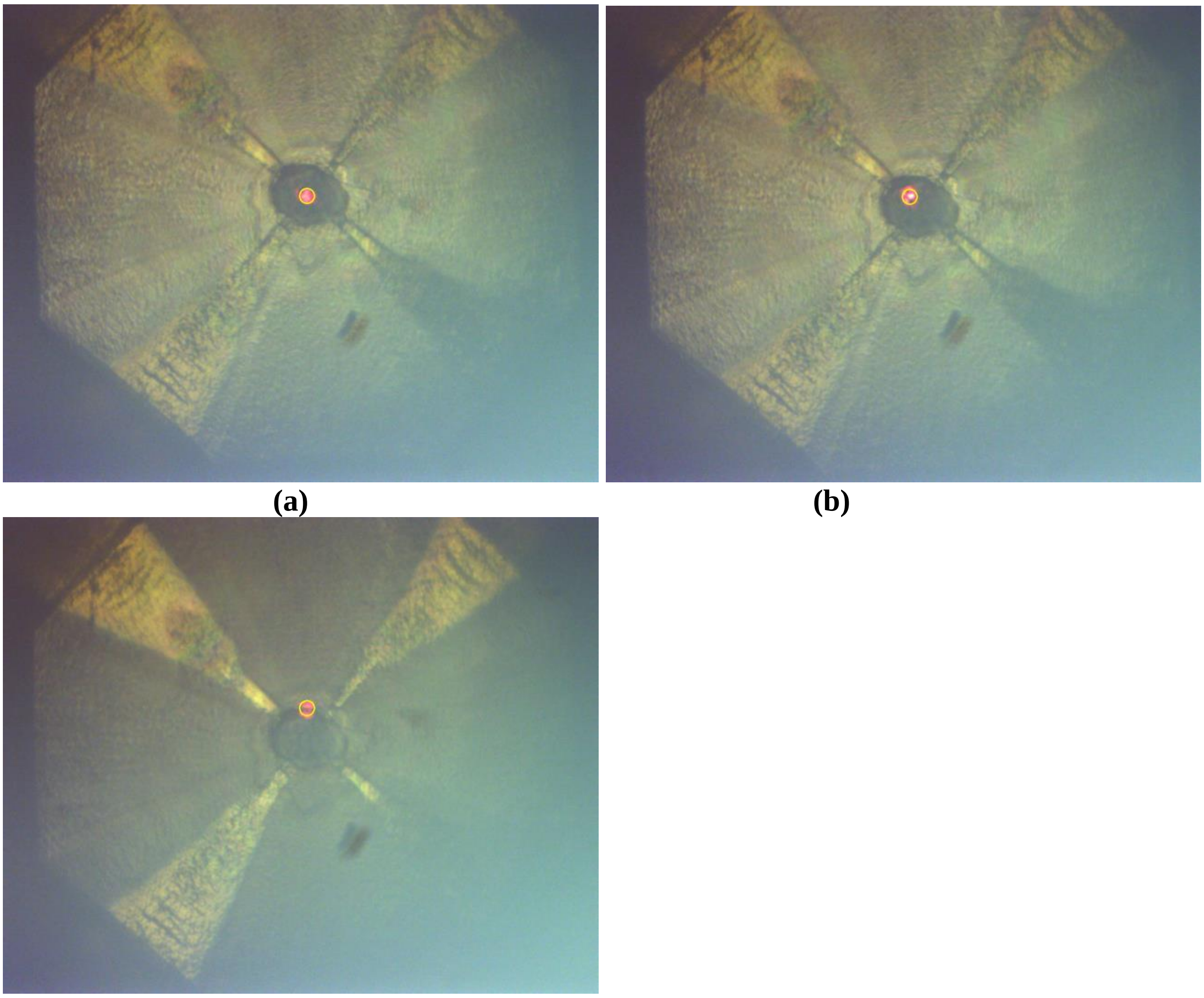


Figure 5. Raman spectra from a diamond anvil, obtained under different conditions: 33.5 - GPa PES-5 medium, 109 GPa - without medium on a cubic boron nitride gasket, 130 GPa - medium and sample are molecular nitrogen.

The more hydrostatic and "softer" the medium, the lower the pressure gradient in the working volume and the sharper and stronger the right edge of the spectrum from which pressure is determined.


(a) **(b)**

(c)

Figure 6. Photographs of the experimental assembly with the points at which Raman spectra from the diamond anvil were taken: (a) in the center of the sample, (b) at one of the contacts, (c) at the edge of the sample.

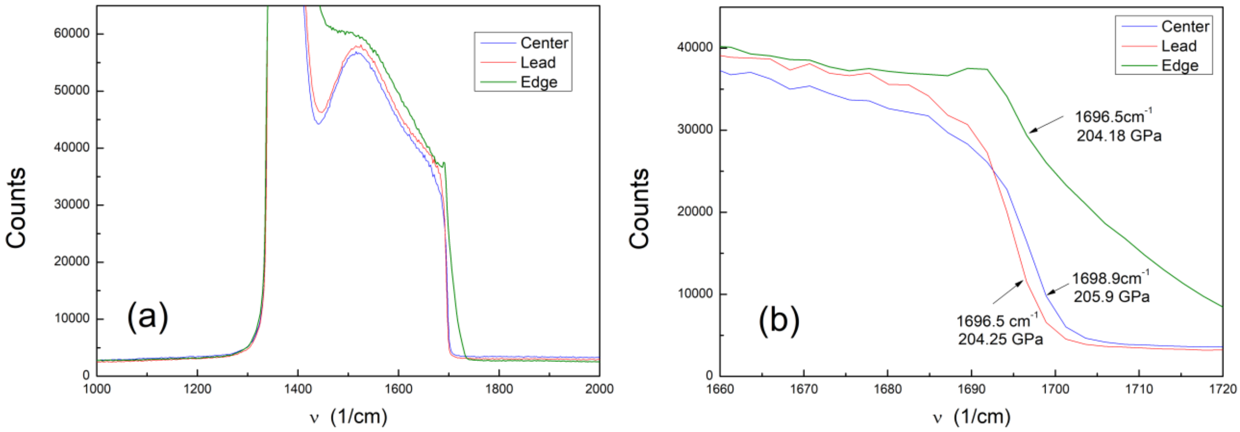


Figure 7. Raman spectra from a diamond anvil and corresponding pressures on the Akahama scale: (a) full spectra, (b) part of the spectra in the right edge region. Point designations: center – central point, lead – point on the contact, edge – point on the edge.

Figure 6 shows, as an example, photographs of the points at which the pressure in the cell was measured (P ~ 200 GPa). Figure 7 shows the Raman spectra taken at these points. The pressure difference at points is no more than 2 GPa, the accuracy of determination at the edge of the spectrum is no worse than 0.5 GPa.

It is obvious that the Raman spectra have an intense sharp right edge and correspond to a fairly "soft" medium. The pressure difference across the sample is no more than 2 GPa. This is a very good result for pressures of ~200 GPa. Thus, we can well claim that we determine the pressure with an accuracy of no worse than 5 GPa, provided that the cooling-heating cycle in a cryostat, as a rule, increases the pressure by no more than 2-5 GPa.

[1]. Y. Akahama and H. Kawamura, Jour. Appl. Phys. **100,** 043516 (2006).