Experimental data at high PT and its interpretation: the role of theory

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Abstract
Experiments, relevant for planetary science, are performed often under extreme conditions of pressure and temperature. This makes them technically difficult. The results are often difficult to interpret correctly, especially in the cases when experimental data are scarce and experimental trends difficult to establish. Theory, while normally is inferior in precision of delivered data, is superior in providing a big picture and details behind materials behavior. We consider the experiments performed for deuterium, Mo, and Fe. We demonstrate that when experimental data is verified by theory, significant insight can be gained.
Keywords: Earth's Inner Core, Molecular Dynamics, Iron, Mo, Deuterium.

Datos experimentales a alta PT y su interpretación: el papel de la teoría

Resumen
Importantes experimentos para la ciencia planetaria se llevan a cabo bajo condiciones extremas de presión y temperatura. Esto hace que sean técnicamente arduos. Los resultados son a menudo difíciles de interpretar correctamente, especialmente cuando los datos experimentales son escasos y la tendencia experimental difícil de establecer. La teoría, aunque tenga normalmente una precisión inferior a los datos observados, es superior en proporcionar un panorama general y detalles que van más allá del simple comportamiento de los materiales en estudio. Considerando los experimentos llevados a cabo para el deuterio, Mo y Fe se demuestra que cuando los datos experimentales están verificados por estudios teóricos se consigue alcanzar un grado de conocimiento más alto.
Palabras clave: Núcleo interno de la Tierra, Dinámica molecular, Hierro, Mo, Deuterio.

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The Earth's deep interior is inaccessible for direct measurements of chemical and phase compositions. This has to be established from comparison of seismic measurements and the data on materials that can be plausibly assumed to constitute the Earth's interior. The data on materials can be measured or computed. The latter way recently gained considerable trust because of advance of theory, software and hardware. The measurements become more difficult and less reliable as the pressure and temperature of experiment increases while the theory reliability remain the same and sometimes even increases due to localization of electrons with pressure.

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Therefore, at some point one can expect that theoretical results shall become more trustworthy than experimental. This might seem to contradict the general paradigm of science of experiment supremacy, but, in fact, it does not. The experimental fact has to be independently verified by alternative techniques and to be solidly established beyond any doubt. Only then, if theory is not in compliance with experiment, something should be done about theory. In this paper we demonstrate that in some cases, even when the experimental data seems to be correct, its interpretation is likely not. When theoretical data is considered along with an experiment, the experiment receives the explanation that could not be obtained from the experimental data alone.

Recently, meticulous shock compression experiments on deuterium have been performed in the pressure range from 45 to 220 GPa (Hicks *et al.*, 2009). The new data provided a maximum compression in the range of 4.8 to 5.0 (with large error bars, though). Thus, the previous radiography measurements as well as the M. Ross model that explains them have been dismissed (for the references see the Ref. (Hicks *et al.*, 2009) unless mentioned otherwise). On the other hand, the data by Knudson *et al.*, 2003 with co-authors also seems to provide too low a compression (about 4.2 as the maximum compression). The Hicks *et al.*, 2009 paper does not seem to provide a satisfactory explanation for this as well as to other features of the Hugoniot adiabat shape.

Direct simulations of shock wave propagation have proved to be a valuable tool for understanding the processes in and behind shock waves (Belonoshko, 1997 and Holian, 1995). To find out the reasons for the controversy between the impedance-matching (IM) and radiography (R) methods, we performed direct MD simulations of the shock-wave propagation in D_2. Note the difference between simulated and calculated – we simulated the whole process of shock wave compression and know all the details that lead to the particular point on the Hugoniot. Fig. 1 shows the comparison of the loci of the simulated Hugoniot data-points compared to the previous and recent (Hicks *et al.*, 2009) data. We see that the predicted Hugoniot actually goes through the cloud of experimental points. We predicted a maximum compression of 4.75 (in fact, in excellent agreement with another theoretical paper of Bezkrovniy *et al.*, 2004 and in some disagreement with a path integral Monte Carlo method of Militzer *et al.*, 2000).

The authors speculate why the Hugoniot exhibits a maximum for compression that sets in 'abruptly'. The answer is simple. When the projectile velocity is sufficient to generate pressures on the level of 100 GPa behind the shock wave front, some of the D_2 molecules dissociate. Energy is spent for the dissociation, therefore the temperature does not increase as fast as it did in the molecular regime. The dissociation makes the material more compressible. Besides, temperature and density increase both facilitate dissociation, therefore their synergetic effect provides impression that the dissociation sets in abruptly. However, it is also possible that the instability, related to the dissociation might interfere in the quality of the data. On further increase of the velocities of impact, the material approaches the ideal gas limit where the compression is equal to 4.

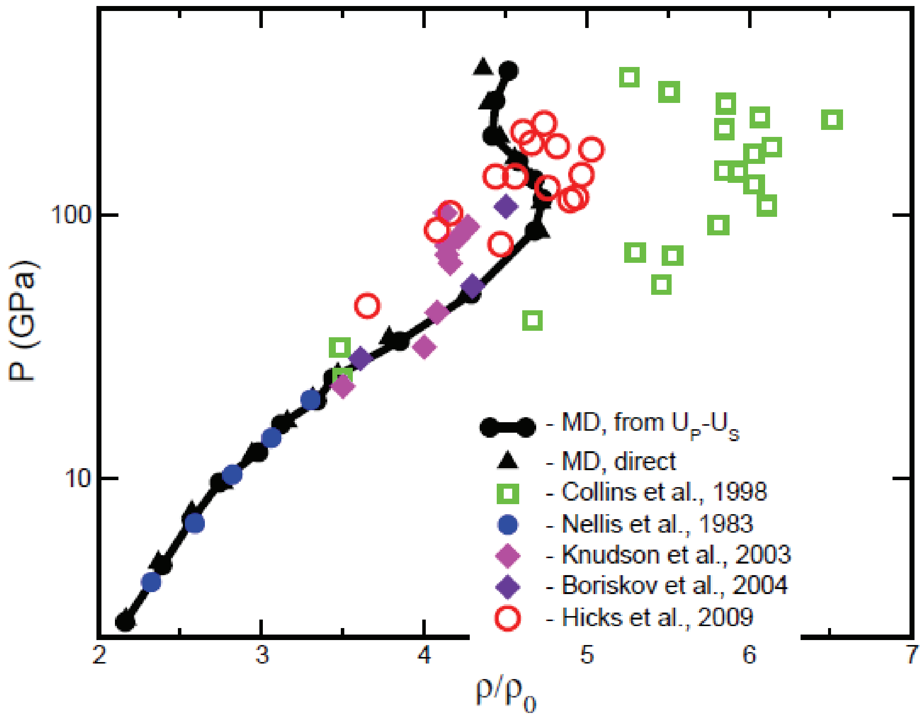

Fig. 1. The new experimental data on D_2 compression (large circles) as compared to our predictions (open triangles and circles) as well as to the experimental data from other sources. The data by Militzer & Ceperley, 2000 is in agreement with the Knudson *et al.* 2003 data, while Bezkrovniy *et al.*, 2004 closely matches ours (4.74 *vs.* 4.75 maximum compression).

Further, the authors do not have a satisfactory answer to the related issue, namely why the R and IM methods provide significantly different results. We see (Fig. 1) that in the range of about 100 to 200 GPa the shock wave front becomes unstable (Belonoshko, 2005). The signature of this is the unusual shape of the adiabat, as was noticed by Dyakov and Kontorovich (see references in Belonoshko *et al.*, 2005). The instability manifests itself in a broadening of the shock wave front. Therefore, the IM technique measures the very first arrival of the shock wave (and, thus, a high shock wave speed) while the R method measures the dense, comparably slow part of the shock wave front. The fast shock provides stiff deuterium and the slow shock provides soft deuterium. It is worth mentioning that the instability, indirectly confirmed by Hicks *et al.*, 2009 might interfere with the highly symmetric compression of the fuel in the inertial fusion experiments at the National Ignition Facility. The behavior of the instability is largely unpredictable, the compression might be asymmetric and hinder the desirable way of operation. Summarizing, this is a nice example when theory, if considered, allows to explain two seemingly conflicting experimental data sets and provide insight into the studied experimentally phenomenon.

In a recent paper (Ruiz-Fuertes, *at al*., 2010) authors argued that Ta melting curve is flat. To confirm that, they provided photos of a Ta sample subject to pressure of 13 GPa and temperatures of 300 K, 3300 K and 3700 K as well as SEM imges for the same sample. They argue that these pictures confirm the flat Ta melting curve. We note that the conditions for taking the photo (13 GPa and 3700 K) belong to the 'high' melting curve (Fig. 3 in the paper), therefore regardless what is shown on the pictures, they cannot be an evidence for the flat melting curve. The authors made measurements up to 48 GPa, however, they have chosen not to show the pictures at high P, where the melting T, according to authors, is indeed very different from the 'high' melting curve (3400 K to 3700 K vs. 4600 K at 48 GPa). Thus, the paper contains no evidence for the low melting curve of Ta.

It has been argued (Belonoshko *et al*., 1997; Belonoshko *at al*., 2000; Belonoshko *et al*., 2004; Belonoshko *et al*., 2008) that 'low' melting curves are likely due to failure of material in DAC. In Mo, this failure is likely facilitated by the approach to the temperature induced solid-solid transition. The discovery of the solid-solid transition in Mo was confirmed independently (Cazorla *et al*., 2008) even though the structure of the emerging phase has been a subject of debate (Cazorla *et al*., 2008; Mikhaylushkin *et al*. 2008). The mechanism of failure was recently independently confirmed by Wu *et al*., 2009, who found that Ta flows under shear at exactly the conditions of the 'flat' melting curve. However, at hydrostatic conditions they find the 'high' melting curve. The authors, unfortunately, misunderstood the theory in the papers cited above and provided distorted account of the current state of theory concerning Ta melting.

Another experiment has been performed to examine the phase diagram of Fe-Si at high pressure (Lin *et al*. 2009). The authors observed that while both *hcp* and *bcc* iron phases alloyed with silicon are present up to 170 GPa, only *hcp* phase could be found above 170 GPa. The experiment was performed up to 240 GPa and 3000 K. Based on this observation, the authors concluded that, contrary to other experiments and theory, the *hcp* phase is stable in the Earth's inner core. In fact, the observations are in perfect agreement with theory (Belonoshko *et al*., 2003; Belonoshko *et al*., 2006; Belonoshko *et al*., 2009). Indeed, the *bcc* Fe is dynamically stable up to 190 GPa. Therefore, it is in agreement with theory that *bcc* disappears above that pressure. The temperature of 3000 K is insufficient to stabilize it dynamically above 190 GPa. However, it does stabilize at higher temperatures, according to theory. Eventually, the *bcc* becomes more stable than *hcp* which is evident from the higher melting temperature of the *bcc* phase. Alloying by Si further promotes the *bcc* phase stability (Fig. 2). If the authors would have been aware of the mechanism behind the *bcc* phase stabilization, they would not come up with the interpretation that contradicts to theory based on facts that are in compliance with theory.

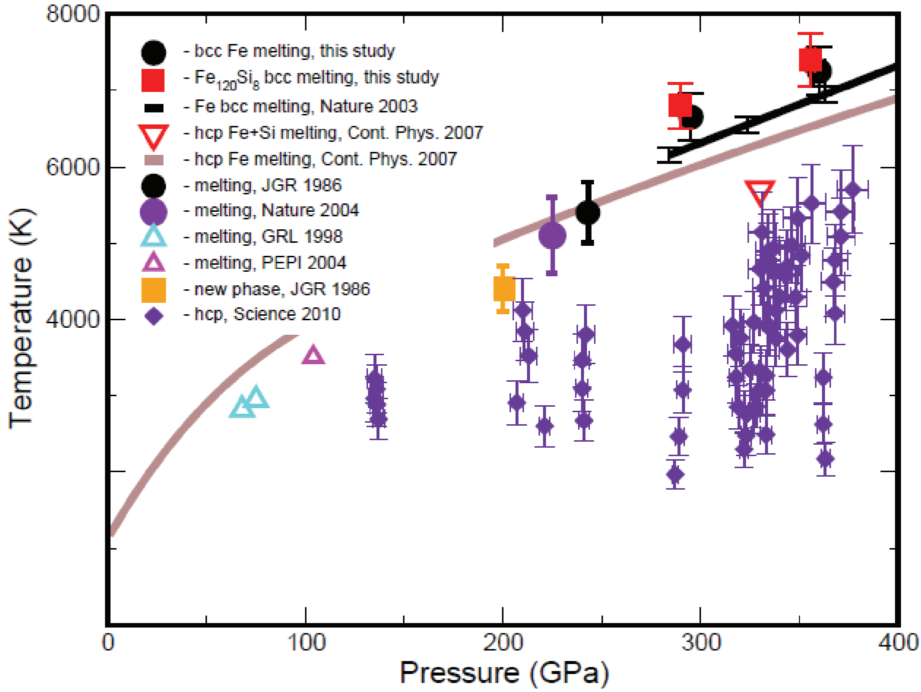

Fig. 2. Iron phase diagram. Computed melting points for pure *bcc* Fe (black circles) and the *bcc* Fe-Si alloy (squares) are shown along with earlier data on the iron phase diagram. The legends provide the stable phase, source, and year of publication. From top to bottom the corresponding references are Belonoshko *et al.*, 2003, Alfè *et al.,* 2007, Brown *et al.,* 1986, Nguyen *et al.,* 2004, Shen *et al.,*1998, Ma *et al.,* 2004, Tateno *et al.,* 2010.

A very recent experimental study (Tateno *et al.*, 2010) claims to study iron phase stability all the way up to its melting. Since the only phase the authors observe is *hcp*, their conclusion is that this is the phase which is stable all the way up to the melting temperature. In fact, it is enough to look at the calculated (Belonoshko *et al.*, 2009) melting curve of iron and Si impact on Fe phase diagram (Fig. 2) to see that the measured points are considerably lower than the melting curve. The measured peak temperatures at the surface of the sample are higher than the temperature of samples. Considering that as well as the large reported error bars, the temperatures might be in fact as low as 5000 K. The calculated melting temperatures consistent with shock-wave data (Brown&McQueen, 1986; Brown, 2001; Nguyen *et al.*, 2004). Thus, there is at least 1500 K interval where *bcc* might be stable (and likely more).

In summary, we demonstrated that unawareness of the theory behind the observations leads to ungrounded conclusions. While the observations are in agreement with theory, their interpretation is in odds. It is especially dangerous to extrapolate the measured results to higher pressures and temperatures without insight into the possible caveats of such extrapolation. On the contrary, when such insight is available, extrapolation becomes highly reliable. We hope that the considered examples will encouraged both experimentalists and theoreticians for close interaction.

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