

# Structure of Amorphous Iron at High Pressures to 67 GPa

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## Introduction

The structure of amorphous metals (metallic glasses) is close to that of liquid metals in general [1]. Because iron is believed to be the major component in planetary cores, it is of geophysical importance to study the behavior of liquid iron at high pressure. In contrast to the extensive experimental high-pressure studies of crystalline iron [2-4], there have been no high-pressure studies reported for amorphous iron, presumably because of the unavailability of samples and the difficulties involved in x-ray scattering measurements. Amorphous iron of high purity has been successfully synthesized sonochemically [5]. Neutron scattering has been used to study the structure of the amorphous iron at ambient pressure [6]. The structure of thin films of amorphous iron has been investigated by using transmission electron diffraction [7, 8]. Here we summarize the results of a room-temperature compression study on amorphous iron up to 67 GPa done by using a monochromatic synchrotron beam and a modified diamond anvil cell (DAC) suitable for studies of amorphous materials at very high pressures. The detailed description is published elsewhere [9].

## Methods and Materials

The amorphous iron sample was prepared sonochemically [5]. Bulk elemental analysis determined the iron powder to be >96 wt% iron with a trace amount of carbon (< 3 wt%) and oxygen (< 1 wt%). The sample can be easily oxidized. Therefore, the sample loading was performed in a glove box filled with inert gas (argon), which provides an atmosphere of <1 part per million (ppm) O<sub>2</sub>. A boron nitride seat was employed for high x-ray transmission over the full aperture of the DAC. The DAC used in this study is a symmetrical cell [10] with a full access opening angle of 60°. Type-IA diamond was used for the anvils, with a culet size of 300 μm in diameter. A stainless steel gasket with an initial thickness of 250 μm was used and preindented to a thickness of ~30 μm. A hole of 300 μm in diameter was drilled and then filled with amorphous boron epoxy (epoxy to boron ratio of 1:2 by weight). The filled boron epoxy was then compressed by diamond anvils to a few gigapascals, and a 100-μm hole was drilled in the pressed boron epoxy. Finally the amorphous sample was loaded in the hole. A few ruby chips were also loaded for pressure measurement. The whole

assemblage was sealed in a glove box by increasing pressures to a few gigapascals. The boron insert gasket helps to collect weak x-ray scattering from amorphous materials free of contamination from gasket diffraction. It also helps to make reliable background subtraction by using the empty cell, without worries about gasket hole deformation. After a maximum pressure of 67 GPa was reached, the pressure was released and the sample was removed from the gasket hole. The same gasket was then put back in the cell, and the empty cell reference was measured with geometry identical to that at high pressures.

X-ray diffraction experiments were performed at beamline station 13 BM-D at the APS. We used a 1-m-long focusing mirror in the vertical direction and a 0.1-m-long mirror in the horizontal direction to focus the beam at the sample position to a size of 10 μm (horizontal) × 27 μm (vertical) at full width at half-maximum (FWHM).

## Results and Discussion

The structure factor  $S(Q)$  and the pair distribution function  $g(r)$  at high pressures are summarized in Fig. 1. The maximum momentum transfer  $Q_{max}$  of 86.6 nm<sup>-1</sup> is used to derive  $g(r)$  for all pressures, including that at ambient pressure. It was found that with increasing pressure, the peak height of  $S(Q)$  [Fig. 1(a)] remains essentially the same, although the peak position shifts to a higher  $Q$  value. Similar features were found in  $g(r)$  in real space. The peak height in  $g(r)$  does not significantly change with an increase in pressure, while the peak position shifts to a smaller  $r$  values, an indication of compression. With the concept of the nearest coordination number (CN), we may describe the picture of the nearest-neighbor atoms in a quantitative way. No clear CN change is found with an increase in pressure within experimental uncertainties, a result consistent with the observation that the peak height and the peak width in  $g(r)$  do not change significantly with pressure.

The general structural feature of the amorphous state is similar to that of the liquid state except for a few weak peaks. In the liquid state, the amplitude of the atomic vibration is large, leading to a large uncertainty in the position of the lattice point, thus resulting in an averaged smooth distribution in both  $S(Q)$  and  $g(r)$ . On the other hand, the small amplitude

of vibration of the atoms in the amorphous state contributes to the construction of a more fixed atomic arrangement, causing some small peaks in  $S(Q)$  and  $g(r)$ .

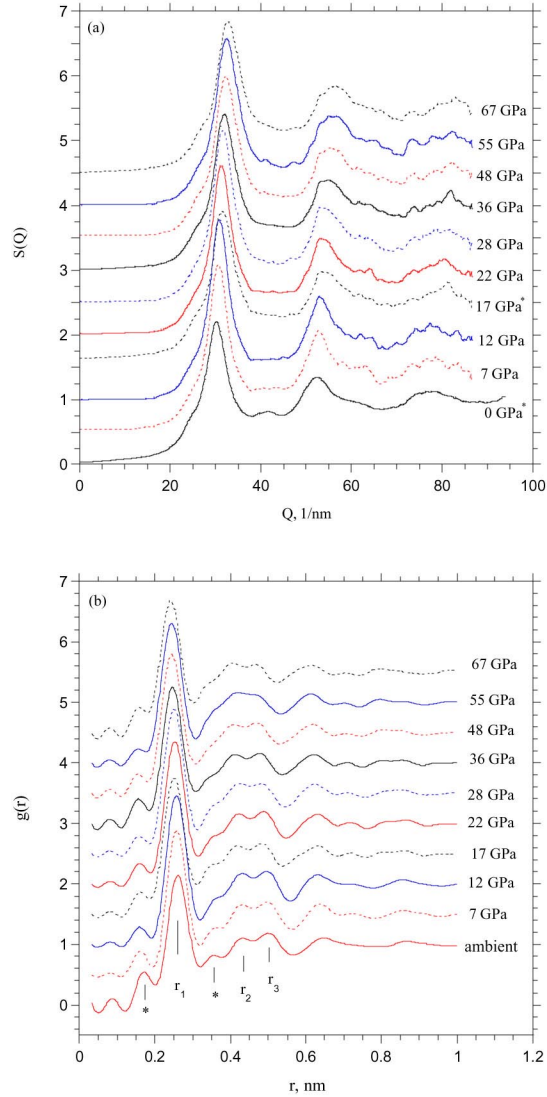


FIG. 1. (a) The structure factor  $S(Q)$  at high pressures. (b) The pair distribution function  $g(r)$  at high pressures. An offset of 0.5 in both  $S(Q)$  and  $g(r)$  is applied between pressures for clarity. Peaks marked with an asterisk are those that might arise from the truncation effect. No clear change in shape or intensity is observed for the dominant first peak in  $S(Q)$  and  $g(r)$ , while the peak positions vary with pressure.

Our data support the concept of a truly amorphous phase devoid of crystalline order on the basis of the following findings. No noticeable change in shape is observed in  $S(Q)$  or  $g(r)$  with an increase

in pressure. These observations disfavor the microcrystalline disorder model because crystalline iron undergoes a phase transition at around 12 GPa (bcc to hcp phase transition), and the phase change would affect the pattern shape and the radial distances in  $g(r)$  according to the calculations of Ichikawa [7].

Our data also imply that the contraction of the amorphous iron is isotropic under pressure. One feature of our high-pressure data is that the dominant peak, both in  $S(Q)$  and  $g(r)$ , does not significantly change with an increase in pressure, except that the peak position shifts to a higher  $Q$  value and to a smaller  $r$  value. This observation is further confirmed by the derived coordination number and ratios of distances. By applying the hard-sphere model, coupled with the Percus-Yevick equation [11], to fit the first peak in  $S(Q)$ , we obtained an almost constant packing fraction of  $0.43 \pm 0.01$  for all pressures up to 67 GPa.

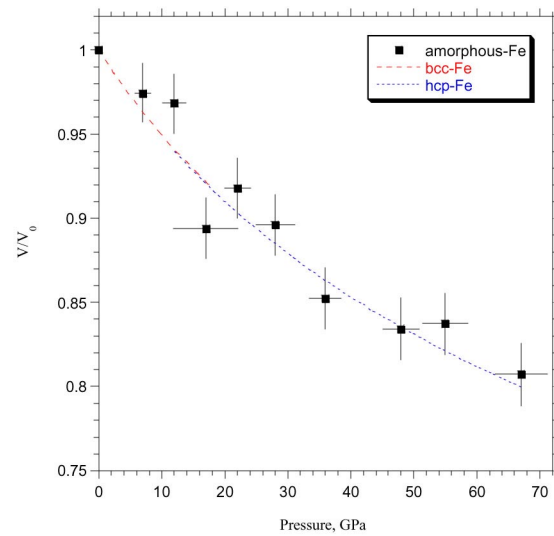


FIG. 2. High-pressure volume compression of amorphous iron measured by the peak shift of the first peak in  $g(r)$ . The validity of using the peak shifts to represent the volume changes is based on the constant packing fraction as a function of pressure. The overall compression is comparable to the behaviors of bcc-Fe and hcp-Fe.

The isotropic contraction makes it possible to estimate densities of amorphous iron at high pressures. Figure 2 shows the plot of  $V/V_0 = r_1^3 / (r_1^3)_{\text{ambient}}$ , with  $r_1$  the position of the first peak in  $g(r)$ , as a function of pressure compared with the compression behaviors of bcc-Fe [2] and hcp-Fe [3]. Error bars in volume are from uncertainties in the peak fitting with a Gaussian function. Pressure error

bars are from the gradients within 30  $\mu\text{m}$  around the sample center. The overall compression is comparable to the behaviors of bcc-Fe and hcp-Fe. The data appear to be too scattered to fit with an equation of state. The scattering of data could be a result of the stress effect arising from the pressure gradient, because no pressure medium was used in the present study to avoid unwanted scattering from other materials. The broad peak in  $g(r)$  also limits the precision in determining the peak position.

## Acknowledgments

Thanks are due to J. Jackson, J. Nicholas, and S. Sinogeikin for their help during sample loading and to P. Eng for help in x-ray scattering experiments. This work is supported by the National Science Foundation (NSF) Grant Nos. EAR 0001149 and 0229987. The GSECARS sector is supported by the NSF Earth Sciences Instrumentation and Facilities Program and U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences (BES), Geoscience Program. Use of the APS was supported by DOE BES under Contract No. W-31-109-ENG-38.

## References

- [1] Y. Waseda, *The Structure of Non-Crystalline Materials* (McGraw-Hill Inc., 1980).
- [2] A.P. Jephcoat, H.K. Mao, and P.M. Bell, *J. Geophys. Res.* **91**, 4677 (1986).
- [3] H.K. Mao, Y. Wu, L.C. Chen, J.F. Shu, and A.P. Jephcoat, *J. Geophys. Res.* **95**, 21737 (1990).
- [4] L.S. Dubrovinsky, S.K. Saxena, F. Tutti, S. Rekhi, and T. Lebehan, *Phys. Rev. Lett.* **84**, 1720 (2000); J.M. Brown, J.N. Fritz, and R.S. Hixson, *J. Appl. Phys.* **88**, 5496 (2000); R. Boehler, *Nature* **363**, 534 (1993); G. Shen, H.K. Mao, R.J. Hemley, T.S. Duffy, and M.L. Rivers, *Geophys. Res. Lett.* **25**, 373 (1998); R.J. Hemley and H.K. Mao, *Int. Geol. Rev.* **43**, 1 (2001).
- [5] K.S. Suslick, S.B. Choet, A.A. Cichowlas, and M.W. Grinstaff, *Nature* **353**, 414 (1991).
- [6] R. Bellissent, G. Galli, M.W. Grinstaff, P. Migliardo, and K.S. Suslick, *Phys. Rev. B* **48**, 15797 (1993).
- [7] T. Ichikawa, *Phys. Status Solidi A* **19**, 707 (1973).
- [8] P.K. Leung and J.G. Wright, *Philos. Mag.* **30**, 995 (1974).
- [9] G. Shen, M.L. Rivers, S.R. Sutton, N. Sata, V.V. Prakapenka, K.S. Suslick, and J. Oxley, *Phy. Earth Planet. Inter.* (in press, 2003).
- [10] H.K. Mao, G. Shen, R.J. Hemley, and T.S. Duffy, in *Properties of Earth and Planetary Materials*, edited by M.H. Manghnani and T. Yagi (American Geophysical Union, Washington, DC, 1998), pp. 27.
- [11] N.W. Ashcroft and J. Lekner, *Phys. Rev.* **145**, 83 (1965).