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High-Pressure $\alpha \rightleftarrows \epsilon$ Martensitic Transformation in Iron

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A study of the high-pressure transformation in iron using an opposed-anvil x-ray diffraction apparatus and high-pressure light metallography has shown that the 130-kbar transformation is martensitic. The bcc and hcp phases were found to coexist over a large pressure range, and there is a large hysteresis between the forward and reverse transformation-start pressures. A room-temperature equilibrium pressure for the bcc and hcp phases of 107 ± 8 kbar is proposed, and discrepancies in the current P-T equilibrium diagram for iron are discussed.

INTRODUCTION

Since the shock-wave research of Bancroft *et al.*[1] on the high-pressure transformation of iron, many investigators have examined this 130-kbar transition. Confirmation of the transformation as a hcp structure, referred to as the ϵ phase, was provided by (a) Balchan and Drickamer's static results,[2] and (b) x-ray analysis of the high-pressure phase by Jamieson and Lawson[3] and later by Takahashi and Bassett[4] as well as Clendenen and Drickamer.[5] A further x-ray investigation[6] showed that the effect of pressure on the lattice parameters of iron could be represented as follows:

$$a(\text{bcc}) = 2.866(1 + P/275)^{-0.056},$$

$$a(\text{hcp}) = 2.523(1 + P/325)^{-0.033},$$

$$c/a = 1.603 \pm 0.001.$$

Recently, Wong *et al.*,[7] using electrical resistivity measurements, reported a possible transformation at 80 kbar, far below the much-confirmed 130-kbar transition for pure iron. Keeler and Mitchell[8] recently reported a possible transformation in pure iron at 50 kbar. The present investigation was undertaken to clarify the confusion concerning the high-pressure phase transformation by systematically studying the effect of pressure on pure iron using x-ray diffraction analysis.

EXPERIMENTAL PROCEDURE

All of the diffraction patterns were obtained using opposed diamond anvils pressurized by a piston and cylinder arrangement utilizing high-pressure dry nitrogen, an apparatus which is similar to that developed by Piermarini and Weir.[9] The collimated x-ray beam, approximately 0.07 mm in diameter, was coaxial with the pressurizing force to minimize the effect of any pressure gradient.

Figure 1 is an enlargement of a piece of photographic film which was placed between the pressurizing anvils with the x-ray beam turned on. This technique shows the x-ray beam size at the sample position and the concentricity of the beam with the piston diamond (octagonal feature). The sample thickness after exposure to high pressure was approximately 0.01 mm with a compressed area of 0.5 mm in diameter. The equipment and experimental procedure used in this investigation have been described elsewhere.[10]

Phase-pressure information was obtained by taking a series of diffraction patterns as follows: for ambient and increasing pressures at 10- or 20-kbar increments up to a nominal pressure of 80 kbar (actual pressure was approximately 160 kbar); and for decreasing pressures, again at 10- or 20-kbar increments, down to ambient pressure. Transformation pressures were recorded as a function of nominal pressure. The diffraction patterns were then measured, and interplanar spacing, lattice parameters, and molar volume were calculated. The actual pressures were arrived at by substituting the experimentally determined lattice parameters for bcc iron into the equation developed by Mao *et al.*[6]

High-pressure light microscopy was accomplished using opposed diamond anvils similar to equipment described previously.[11] The equipment was mounted on a standard metallographic microscope with reflected light. A xenon light source was used.

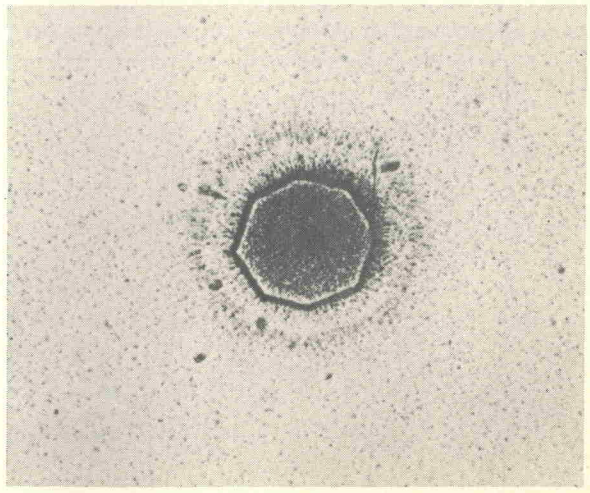
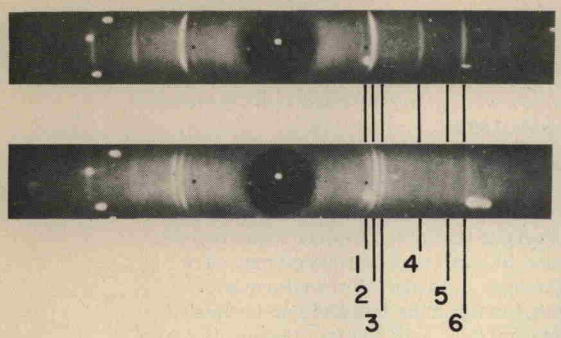


FIG. 1. Enlargement of photographic film placed between pressurizing diamond anvils. The octagonal shaped feature is the impression of the outer edges of the piston diamond. The dark spot in the center was caused by the x-ray beam, which was approximately 0.07 mm in diameter.



LINE	INTERPLANAR SPACING, Å	PHASE AND INDICES
1	2.18	$\epsilon(100)$
2	2.03	$\alpha(110)$ $\epsilon(002)$
3	1.92	$\epsilon(101)$
4	1.43	$\alpha(200)$
5	1.26	$\epsilon(110)$
6	1.17	$\alpha(211)$

FIG. 2. High-pressure diffraction patterns of iron with diffraction lines identified. Upper diffraction pattern was obtained at room pressure and temperature while the lower diffraction pattern was obtained at 169 kbar and room temperature.

RESULTS

Figure 2 shows two of a series of 12 x-ray diffraction patterns obtained from iron at various pressures. These patterns were made using a 0.25-mm-diam x-ray beam on electrolytic iron powder samples (>99.98% Fe). The numbered vertical lines running between the patterns indicate the approximate positions of the diffraction lines which are identified in the table below the patterns; the listed interplanar spacings are for ambient pressure. It can be seen that at 169 kbar, the sample contains a significant amount of the hcp phase (line 3). All of the hcp present at high pressure transformed to bcc before ambient pressure was reached. Table I lists experimental data obtained using a 0.07-mm-diam x-ray beam.

A plot of the effect of pressure on the molar volume of both the bcc and hcp phases is seen in Fig. 3. It is seen that with increasing pressure the hcp phase becomes evident at approximately 133 kbar, a result which is in good agreement with previous investigators.[1-6] However, it should be pointed out that the bcc phase persists to 163 kbar. The amount of bcc present at 163 kbar was estimated to be 40%. On lowering pressure from 81 to 45 kbar, the amount of hcp (ϵ) phase present in the area irradiated by the x-ray beam gradually decreases. The hcp (ϵ) phase completely disappears at 45 kbar.

DISCUSSION

The results shown in Fig. 3 are (i) a large pressure range over which bcc (α) and hcp (ϵ) phases coexist, and (ii) a large pressure hysteresis between the onset of the ϵ transformation on pressurization and the beginning of the α transformation on depressurizing. These results are indicative of a martensitic transformation, and these starts and finishes are therefore marked accordingly in Fig. 3:

start of the $\alpha \rightarrow \epsilon$ transformation, $P_{M_s}^{\alpha\rightarrow\epsilon}$, 133 kbar;

finish of the $\alpha \rightarrow \epsilon$ transformation, $P_{M_f}^{\alpha\rightarrow\epsilon}$, >163 kbar;

start of the $\epsilon \rightarrow \alpha$ transformation, $P_{M_s}^{\epsilon\rightarrow\alpha}$, 81 kbar;

finish of the $\epsilon \rightarrow \alpha$ transformation, $P_{M_f}^{\epsilon\rightarrow\alpha}$, 45 kbar.

It was found that the volume change during the trans-

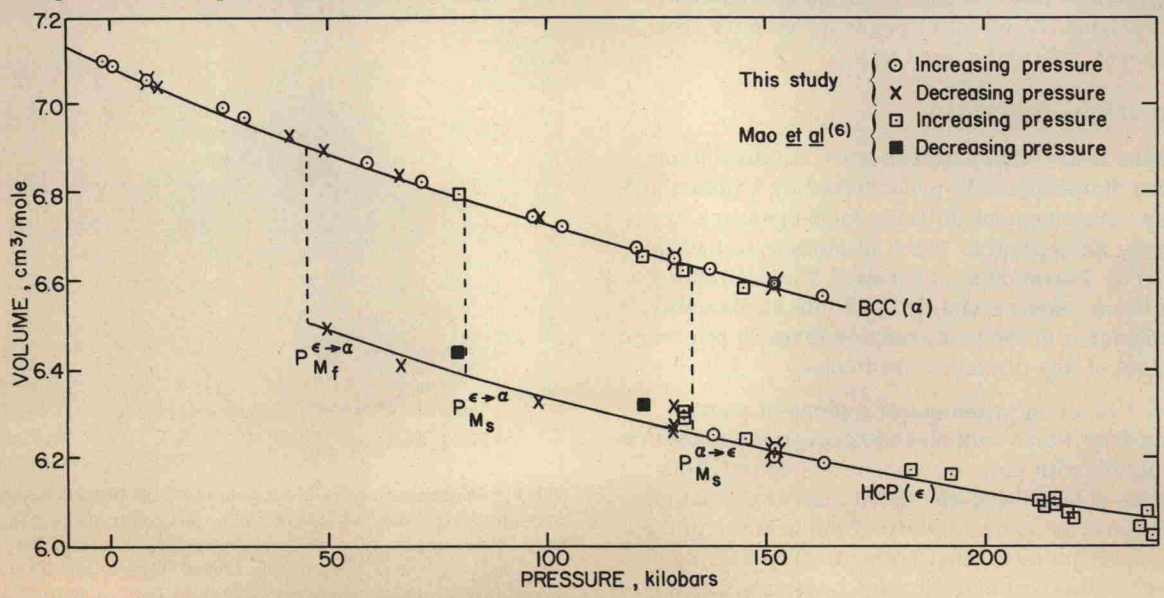


FIG. 3. Effect of pressure on the molar volume of bcc and hcp iron.