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 pressureizing 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.
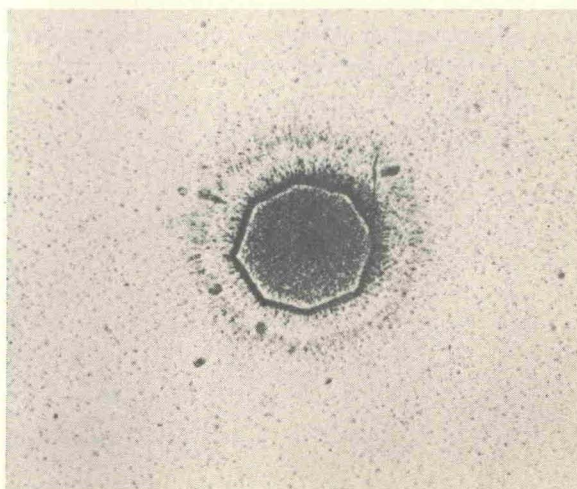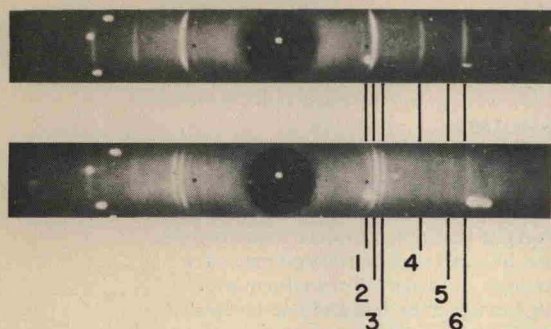

FIG. 1. Enlargement of photographic film placed between pressurizing diamond anvils. The octagonal shaped feature is the impression of the outer edges of the piston diamond. The dark spot in the center was caused by the x-ray beam, which was approximately 0.07 mm in diameter.

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 approxi-mate 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 investiga-tors.[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 on-set of the ϵ transformation on pressurization and the beginning of the α transformation on depressurizing. These results are indicative of a martensitic trans-formation, and these starts and finishes are there-fore 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.

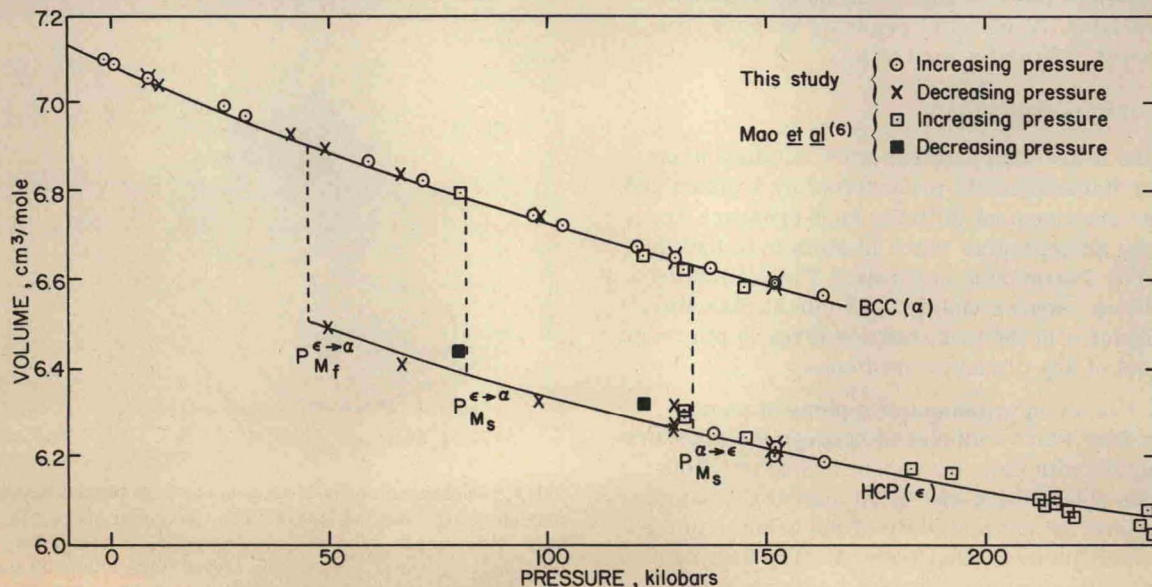It was found that the volume change during the trans-

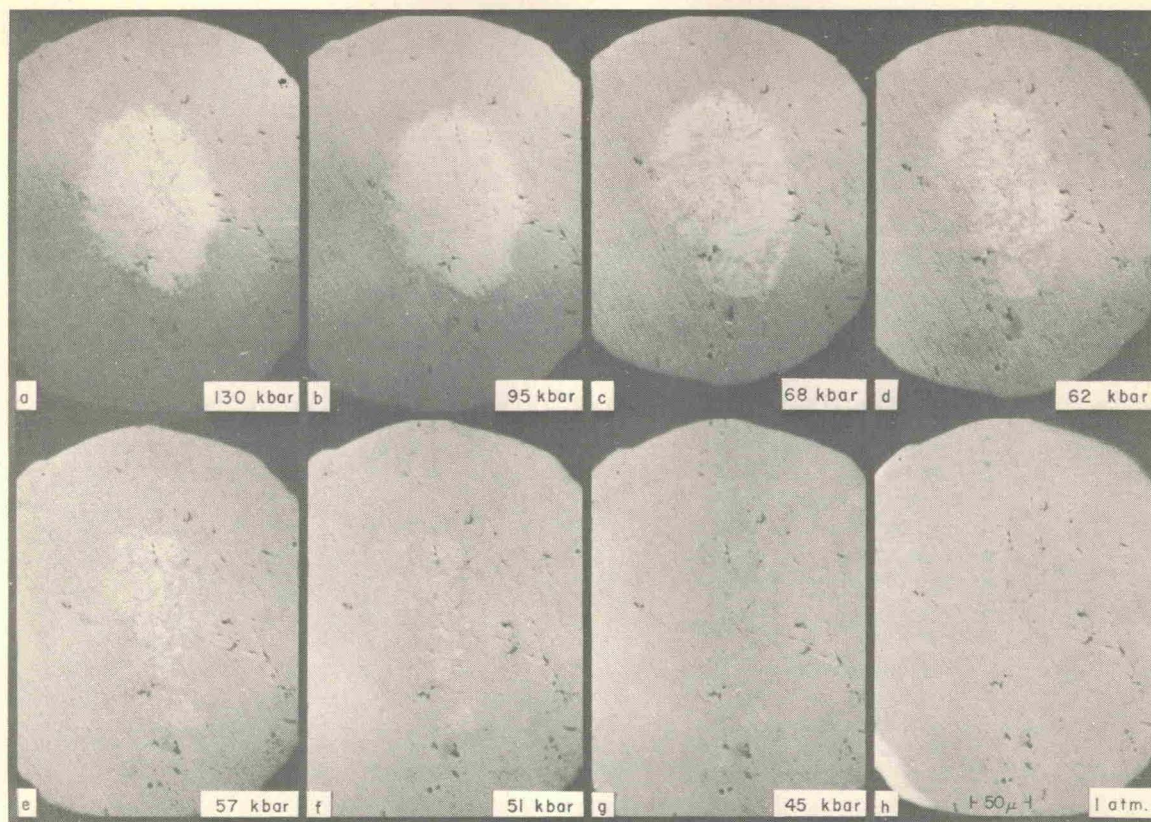FIG. 3. Effect of pressure on the molar volume of bcc and hcp iron.

FIG. 4. Photomicrographs taken in a diamond high-pressure cell of the $\alpha \rightleftarrows \epsilon$ transformation in pure iron.

formation from bcc (α) to hcp (ϵ) was approximately 0.38 cm³/mole at 133 kbar (Table I). Takahashi reported that the volume change during the transformation was 0.34 cm³/mole.[6] This difference can be

TABLE I. Pressure-lattice parameter results.

P (kbar)	a(bcc) (Å)	a(hcp) (Å)	V(bcc) (cm³/ mole)	V(hcp) (cm³/ mole)	ΔV (cm³/ mole)
1	2.866		7.09		
9	2.861		7.05		
26	2.852		6.96		
31	2.849		6.99		
59	2.835		6.86		
71	2.829		6.82		
97	2.818		6.74		
104	2.815		6.72		
121	2.808		6.67		
125	2.807		6.66		
130	2.805		6.65		
137	2.802	2.463	6.62	6.25	0.37
151	2.797	2.458	6.59	6.21	0.38
151	2.797	2.459	6.59	6.22	0.37
163	2.792	2.455	6.56	6.19	0.37
151	2.797	2.455	6.59	6.19	0.40
151	2.797	2.459	6.59	6.22	0.37
129	2.805	2.466	6.65	6.27	0.38
129	2.805	2.466	6.65	6.27	0.38
129	2.805	2.472	6.65	6.31	0.34
98	2.818	2.473	6.74	6.33	0.41
66	2.832	2.484	6.84	6.41	0.43
49	2.840	2.495	6.90	6.49	0.41
41	2.844		6.93		
11	2.860		7.05		
8	2.861		7.06		

accounted for by the experimental error in high-pressure x-ray measurements, since a difference of 0.0027 Å in the determined value of the α (2$\hat{0}$0) line will readily account for a 0.04-cm³ difference in ΔV. The volume change was also found to decrease with increasing pressure above 130 kbar and to increase with decreasing pressure below 81 kbar. This variation in volume change was found to be virtually identical, except for the 0.04-cm³/mole displacement of the curves, with that which can be readily obtained from the information presented by Takahashi et al.[12]

Several investigators have reported that the bcc (α) to hcp (ϵ) transformation occurs over a range of pressures and is apparently very sluggish.[2,5,7] In fact, in a discussion of a paper concerned with the use of iron as a calibration point, Jamieson[13] suggested that the $\alpha \rightarrow \epsilon$ transformation was martensitic, occuring over a range of pressures, and therefore could not be used as a calibration standard. Later, Bowden and Kelly[14] showed from crystallographic analysis of shock-loaded iron that the α to ϵ to α transformation was martensitic. They stated that "any phase transformation which occurs under shock loading must be martensitic." Recently, a study of the $\alpha \rightarrow \epsilon$ transformation in Fe-Ni-Cr alloys that was based on the use of prepolished surfaces in a large hydrostatic pressurization apparatus showed surface shears characteristic of a martensitic transformation.[15]
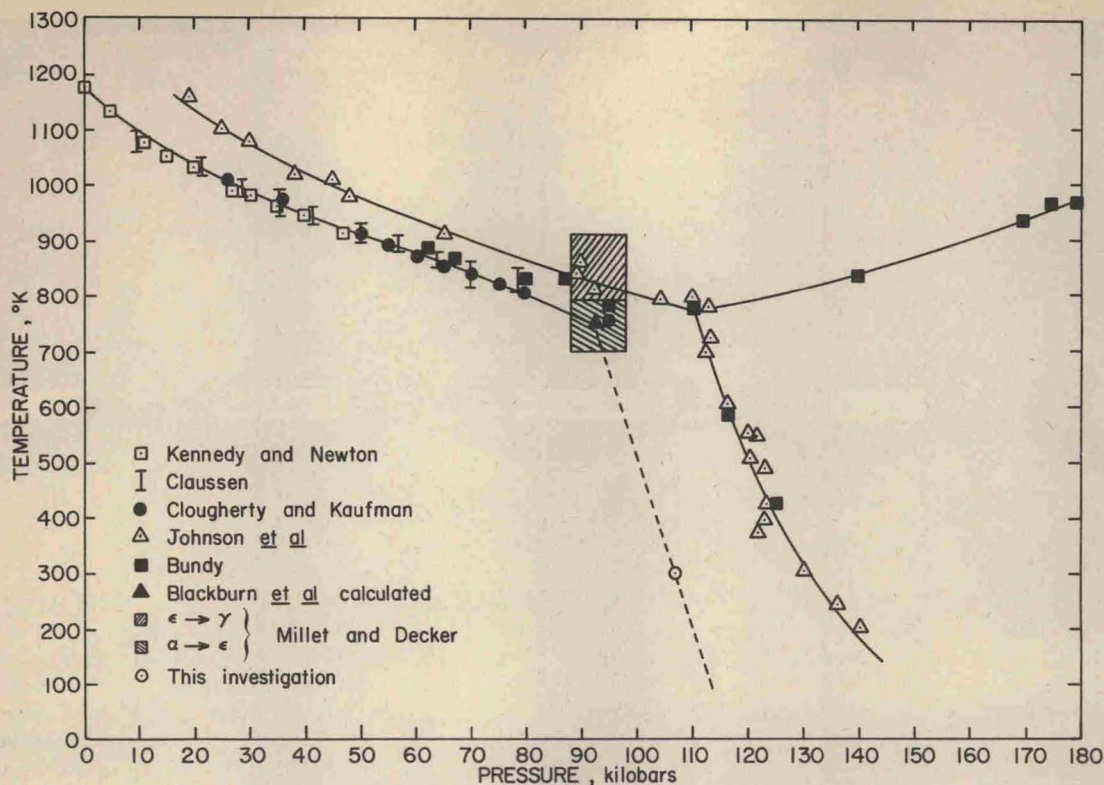
FIG. 5. Pressure-temperature diagram for pure iron.

A further proof that the $\alpha \to \epsilon$ phase change under pressure has all the features of a martensitic transformation is evidenced in Fig. 4. In this figure, pure iron was subjected to a high hydrostatic pressure in a diamond high-pressure cell under a light microscope. Although the pressure was unknown on an absolute basis, on the basis of the nominal load/area pressure relationship the hysteresis for the forward and reverse $\alpha \rightleftarrows \epsilon$ transformation was considerable. In the case of Fig. 4, ϵ has already formed and is identified as the central white region in Fig. 4(a). It can be seen that as pressure is released, the reverse transformation ($\epsilon \to \alpha$) occurs within specific areas, rather than through the motion of a phase front, a mode which is typical of an equilibrium-type transformation. In an equilibrium type of transformation, as pressure increases, an island at the center of the diamonds spreads out, forming a ring that represents a boundary between two phases that have different indices of refraction.[16] However, for iron, as in the case of the martensitic transformation, independent areas transform simultaneously, producing a mottled effect. An analogy can be drawn from hot-stage microscopy studies of the martensite transformation in an Fe-C alloy.[17] Only when sufficient pressure is supplied so that the martensite finish pressure $P_{m_f}^{\alpha \to \epsilon}$ is exceeded, does the mottled effect disappear (Fig. 4). This sequence of results also shows that the martensitic $\alpha \to \epsilon$ tranformation is an "abaric" one, in which the transformation will proceed only when pressure is changed. (In

this usage the term "abaric" is analogous to "athermal".) It was found that upon holding at pressure, no change in the amount of phases present occurred.

Since the bcc (α) to hcp (ϵ) phase change in pure iron has the characteristics of a martensitic transformation, an analogy can be drawn between the determination of the equilibrium temperature T_0 and the determination of the equilibrium pressure between the two phases. In considering temperature, Kaufman and Cohen[18] defined T_0 as the temperature where $\Delta F(T) = 0$ at constant pressure, which can be calculated by bracketing the martensitic forward and reverse temperatures in the case of the austenite (fcc) to martensite (bcc) transformation:

$$T_0 = \tfrac{1}{2}(T_{M_s}^{\gamma \to \alpha} + T_{A_s}^{\alpha \to \gamma}),$$

where $T_{M_s}^{\gamma \to \alpha}$ is the martensitic start temperature in the fcc (γ) to bcc (α) transformation and $T_{A_s}^{\alpha \to \gamma}$ is the austenitic start temperature in the bcc (α) to fcc (γ) transformation. Thus, for the pressure analog, the equilibrium pressure P_0 is defined as the pressure where $\Delta F(P) = 0$ at constant temperature. It should also be possible to determine this value by bracketing the martensite forward and reverse pressures, as in the case for the bcc (α) to hcp (ϵ) transformation. Thus, we have

$$P_0 = \tfrac{1}{2}(P_{M_s}^{\alpha \to \epsilon} + P_{M_s}^{\epsilon \to \alpha}),$$

where $P_{M_s}^{\alpha \to \epsilon}$ is the martensitic start pressure for the

bcc (α) to hcp (ϵ) transformation and $P_{M_s}^{\epsilon \to \alpha}$ is the reverse martensitic start pressure for the hcp (ϵ) to bcc (α) transformation. A calculation of P_0 from the data shows that the equilibrium line at 300 °K is at 107 ± 8 kbar rather than at the previously reported 130 kbar,[1-6] which, as the present study shows, should be regarded as the martensitic start pressure.

According to Blackburn et al.,[19] at 300 °K and 1 atm, bcc iron is 1010 cal/mole more stable than hcp iron. Hence, the product of (23.9) $P_0 \Delta V$ should be equal to -1010 cal/mole. Substituting $\Delta V = 0.38$ cm^3/mole and solving for P_0 yields an equilibrium transformation pressure of 111 kbar. This value is in excellent agreement with the experimentally determined value of 107 ± 8 kbar, considering that an approximation was made for the $P_{M_s}^{\epsilon \to \alpha} = 81$ kbar by averaging the determination at 98 kbar, where no increase in bcc was found and the determination at 66 kbar where an increase in bcc was found. Further confirmation of the equilibrium transformation pressure P_0 is indicated from a calculation of the driving force for the bcc→ hcp reaction. This force can be estimated by multiplying 23.9 by ΔV, the difference in pressure between the $P_{M_s}^{\alpha \to \epsilon}$ and $P_0^{\alpha \to \epsilon}$. Again, using $\Delta V = 0.38$ cm^3/mole and a pressure difference of $133 - 107 = 26$ kbar, a driving force of 227 cal/mole is obtained, which is in good agreement with determined values of 150–300 cal/mole calculated for the martensite transformation in iron alloys.[18]

Given the data of the present study, a triple point of 775 °K and 110 kbar[20,21] for the pressure-temperature equilibrium diagram of iron with a P_0 of 107 kbar for the $\alpha \rightleftarrows \epsilon$ transformation cannot be justified in thermodynamic terms. A review of the various methods others have employed to determine the triple point is therefore in order. Using shock pressure techniques and microstructural observations, Johnson et al.[20] found an inflection point, later the triple point, in the transformation curve at 775 °K and 115 kbar. However, not realizing that they were dealing with a possible $\alpha \rightarrow \epsilon$ matrensitic transformation they normalized their observed pressure to 130 kbar at room temperature and assumed that the microstructure is associated with the pressure necessary to initiate the phase transformation. Later, Bundy[21] made electrical reistivity measurements to determine the P-T diagram and established a triple point at (763 ± 10) °K and 100 ± 3 kbar. Bundy calibrated his triple point with the Johnson et al.[20] data, which he "accepted as being correct on an absolute basis because of the correlation with the 130-kbar, room-temperature $\alpha \rightarrow \epsilon$ transition, which has been established with considerable certainty."

The data of Johnson et al.[20] and Bundy[21] are plotted in Fig. 5 along with the data on the $\alpha \rightarrow \gamma$ transformation by Kennedy and Newton[22] by Claussen,[23] and by Clougherty and Kaufman.[24] Also included is the data point of this investigation for the P_0 of the

$\alpha \rightleftarrows \epsilon$ transformation and a triple point of 750 °K and 92 kbar calculated from thermodynamic data by Blackburn et al.[19] The discrepancy in the data on the $\alpha \rightleftarrows \gamma$ branch was attributed by Blackburn et al.[19] to pressure overshooting of the isothermal shock-wave measurements of Johnson et al.[20] This overshooting of pressure, coupled with a reported martensitic start pressure for the $\alpha \rightleftarrows \epsilon$ transformation[20] rather than a P_0, has led to a wrong interpretation of the triple point.[19] Recently, Millet and Decker[20] have reported preliminary data on the Mossbauer spectra near the triple point of iron. Their data, which are included in Fig. 5, indicated to them that the triple point is lower than the reported 110 kbar. These inconsistencies suggest that a reevaluation of the equilibrium pressure-temperature diagram of pure iron is in order.

CONCLUSIONS

The following can be concluded from this investigation: (i) a systematic x-ray study confirms that the transformation of $\alpha \rightarrow \epsilon$ starts at 130 kbar. (ii) The large hysteresis between forward and reverse transformation of the $\alpha \rightleftarrows \epsilon$ and the large pressure range over which the two phases exist are indicative of a martensitic transformation. (iii) Light microscopy of the transformation in a high-pressure diamond cell shows that the hcp (ϵ) phase transforms abarically in a nonuniform manner characteristic of martensite and not as a moving circular phase front common to most transformations seen in the microscope. (iv) The P_0 value for the $\alpha \rightleftarrows \epsilon$ transformation was found to be 107 ± 8 kbar at 300 °K. (v) A reevaluation of the pressure-temperature equilibrium diagram is in order, since the new P_0 value at room temperature places the triple point of 110 kbar and 775 °K in doubt.

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