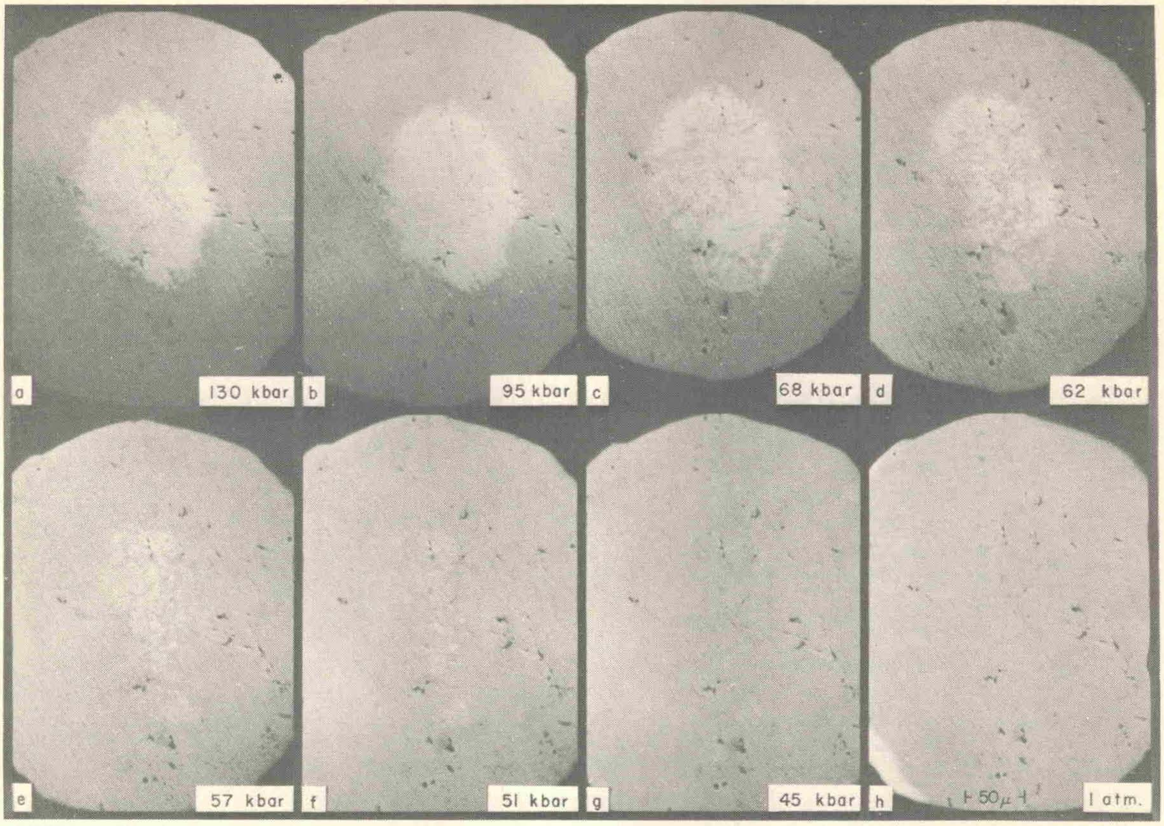

FIG. 4. Photomicrographs taken in a diamond high-pressure cell of the $\alpha \rightleftarrows \epsilon$ transformation in pure iron.

formation from bcc (α) to hcp (ϵ) was approximately 0.38 cm^3/mole at 133 kbar (Table I). Takahashi reported that the volume change during the transformation was 0.34 cm^3/mole.[6] This difference can be 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-cm^3 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-cm^3/mole displacement of the curves, with that which can be readily obtained from the information presented by Takahashi *et al.*[12]

TABLE I. Pressure-lattice parameter results.

P (kbar)	a(bcc) (Å)	a(hcp) (Å)	V(bcc) (cm^3/mole)	V(hcp) (cm^3/mole)	ΔV (cm^3/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		

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]

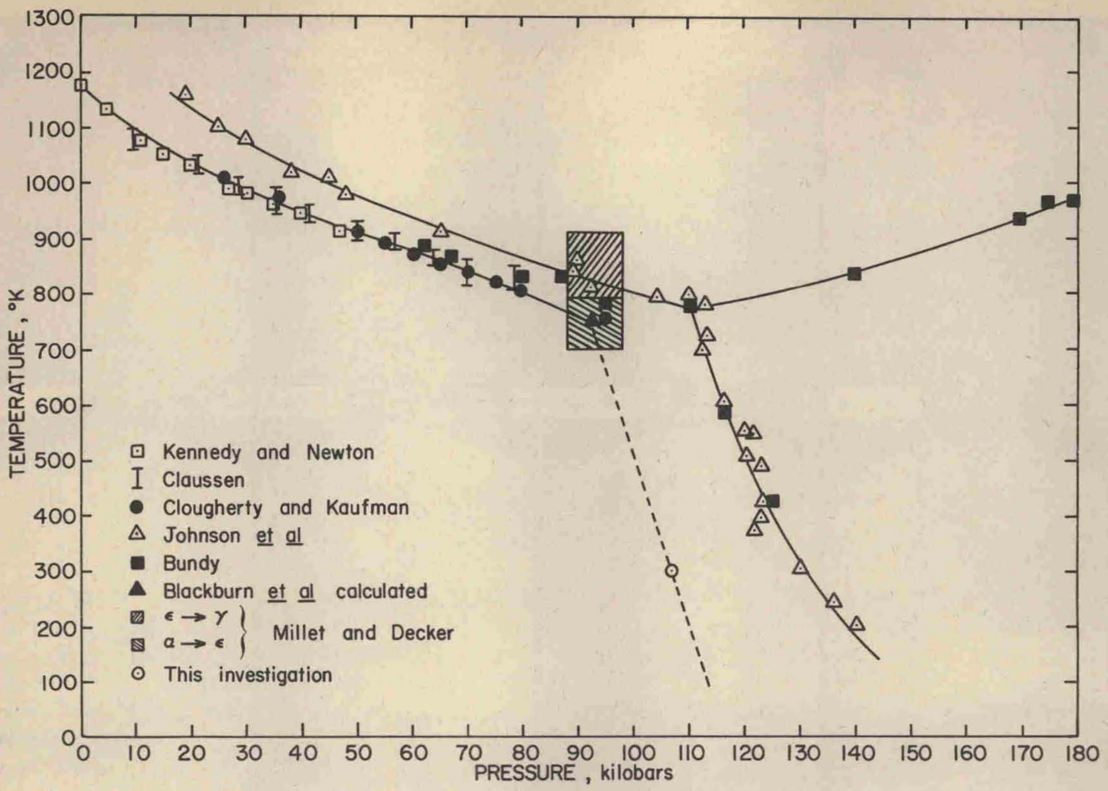

FIG. 5. Pressure-temperature diagram for pure iron.

A further proof that the $\alpha \rightarrow \epsilon$ 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 ($\epsilon \rightarrow \alpha$) 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 $P_{m_f}^{\alpha\rightarrow\epsilon}$ is exceeded, does the mottled effect disappear (Fig. 4). This sequence of results also shows that the martensitic $\alpha \rightarrow \epsilon$ 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:

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

where $T_{M_s}^{\gamma\rightarrow\alpha}$ is the martensitic start temperature in the fcc (γ) to bcc (α) transformation and $T_{A_s}^{\alpha\rightarrow\gamma}$ 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

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

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