

bcc (α) to hcp (ϵ) transformation and $P_{M_s}^{\epsilon \rightarrow \alpha}$ 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 $\Delta V = 0.38$ cm³/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 $P_{M_s}^{\alpha \rightarrow \epsilon} = 81$ 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 \rightarrow hcp reaction. This force can be estimated by multiplying 23.9 by ΔV , the difference in pressure between the $P_{M_s}^{\alpha \rightarrow \epsilon}$ and $P_0^{\alpha \rightarrow \epsilon}$. Again, using $\Delta V = 0.38$ cm³/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 $\alpha \rightleftharpoons \epsilon$ 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 $\alpha \rightarrow \epsilon$ martensitic 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, Bundy²¹ made electrical resistivity 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 Bundy²¹ are plotted in Fig. 5 along with the data on the $\alpha \rightarrow \gamma$ transformation by Kennedy and Newton²² by Claussen,²³ and by Clougherty and Kaufman.²⁴ Also included is the data point of this investigation for the P_0 of the

$\alpha \rightleftharpoons \epsilon$ 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 $\alpha \rightleftharpoons \gamma$ 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 $\alpha \rightleftharpoons \epsilon$ transformation²⁰ rather than a P_0 , has led to a wrong interpretation of the triple point.¹⁹ Recently, Millet and Decker²⁰ 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 $\alpha \rightleftharpoons \epsilon$ 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 aperiodically 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 $\alpha \rightleftharpoons \epsilon$ 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.

ACKNOWLEDGMENTS

The authors would like to acknowledge the technical assistance of R. E. Steigerwalt and R. Kossifos, the high-pressure metallography of A. O. Benscoter, as well as the assistance of B. S. Mikofsky in the preparation of the manuscript. The review of the manuscript by L. Kaufman of ManLabs, Inc. is greatly appreciated.

¹D. Bancroft, E. L. Peterson, and S. Minshall, *J. Appl. Phys.* 27, 291 (1956).

²A. S. Balchan and H. G. Drickamer, *Rev. Sci. Instr.* 32, 308 (1961).

³J. C. Jamieson and A. W. Lawson, *J. Appl. Phys.* 33, 776 (1962).

⁴T. Takahashi and W. A. Bassett, *Science* 145, 483 (1964).

⁵R. L. Clendenen and H. G. Drickamer, *J. Phys. Chem. Solids* 25, 865 (1964).

⁶H. Mao, W. A. Bassett, and T. Takahashi, *J. Appl. Phys.* 38, 272 (1967).

⁷J. Y. Wong, R. K. Linde, and P. S. DeCarli, *Nature* 219, 713 (1968).

- ⁸R. N. Keeler and A. C. Mitchell, *Solid State Commun.* 7, 271 (1969).
- ⁹G. J. Piermarini and C. E. Weir, *J. Res.* 66A, 325 (1962).
- ¹⁰P. M. Giles and M. H. Longenbach, *Proceedings of the Second Annual Meeting of the International Metallographic Society*, 1969, p. 111.
- ¹¹C. E. Weir, A. VanValkenberg, and E. Lippincott, in *Modern Very High Pressure Techniques*, edited by R. H. Wentdorf (Butterworths, Washington, D. C., 1962), p. 51.
- ¹²T. Takahashi, W. A. Bassett, and H. K. Mao, *J. Geophys. Res.* 73, 4717 (1968).
- ¹³J. C. Jamieson in discussion of a paper by E. V. Clougherty and L. Kaufman, in *High Pressure Measurements*, edited by A. A. Giardini and E. C. Lloyd (Butterworths, Washington, D. C., 1963), p. 165.
- ¹⁴H. G. Bowden and P. M. Kelly, *Acta Met.* 15, 1489 (1967).
- ¹⁵P. M. Giles and A. R. Marder, *Met. Trans.* 2, 1371 (1971).
- ¹⁶A. VanValkenberg, in *High Pressure Measurements*, edited by A. A. Giardini and E. C. Lloyd (Butterworths, Washington, D. C., 1963), p. 87.
- ¹⁷A. R. Marder and G. Krauss, *ASM Trans.* 62, 957 (1969).
- ¹⁸L. Kaufman and M. Cohen, in *Progress in Metal Physics*, edited by B. Chalmers and R. King (Pergamon, London, 1958), Vol. 7, p. 165.
- ¹⁹L. D. Blackburn, L. Kaufman, and M. Cohen, *Acta Met.* 13, 533 (1965).
- ²⁰P. C. Johnson, B. A. Stein, and R. S. Davis, *J. Appl. Phys.* 33, 557 (1962).
- ²¹F. P. Bundy, *J. Appl. Phys.* 36, 616 (1965).
- ²²G. C. Kennedy and R. C. Newton, in *Solids Under Pressure*, edited W. Paul and D. M. Warshauer (McGraw-Hill, New York, 1962), p. 463.
- ²³W. Claussen, *Rev. Sci. Instr.* 31, 878 (1960).
- ²⁴E. V. Clougherty and L. Kaufman, in *High Pressure Measurements*, edited by A. A. Giardini and E. C. Lloyd (Butterworths, Washington, 1963), p. 152.
- ²⁵L. E. Millet and D. L. Decker, *Phys. Letters* 29A, 7 (1969).