The martensitic transformation in pure iron

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SYNOPSIS

High-rate quenching experiments have established that iron containing less than 0·0017%C transforms martensitically at 750°C at cooling rates in excess of 35000 degC/s. M_s falls to 540°C, and the critical quenching speed is lowered to 5000 degC/s when the carbon content is increased to a figure between 0·005 and 0·01%. Two hypotheses are offered to rationalize the effect of carbon, and Crussard's shock-wave model of the martensitic transformation is extended. 2275

INTRODUCTION

EVEN when the word martensite was exclusively used to describe the hard transformation product in steels, there was some appreciation that the adjective martensitic could be used with more justification to define a certain type of transformation process. However, due largely to the difficulty of establishing a convenient experimental criterion by which martensitic transformations might be identified, the early work on the subject, reviewed by Troiano and Greninger,[1] does not permit a satisfactory distinction, as Bilby and Christian have pointed out,[2] between martensitic and non-martensitic processes. For example, characteristics such as the constancy of M_s with cooling rate, and the athermal nature of the process, are neither exclusive nor always necessary.

The most adequate and applicable single criterion to identify martensitic transformation is a shape change,[3] revealed by the rumpling of a polished surface, which is caused by the tilting of transformed regions. If one applies this criterion to the photomicrographs taken by Sauveur and Chou[4] in 1929, there is no doubt that the transformation produced in electrolytic iron quenched in mercury from 1000°C was indeed martensitic. However, in 1929, the constitution of martensite was still in doubt; the shear mechanism of formation had not been proposed; transformation temperatures had not, apparently, been measured.

During the last twenty years, investigations of martensitic transformations have concentrated on iron-base alloys that are of industrial importance or experimentally convenient. Arguments pertaining to mode of nucleation and to the distinction between athermal and isothermal characteristics have become largely semantic. A reaction type, designated massive (and intermediate to martensitic and diffusion-controlled transformations), was proposed in 1958 by Massalski[5] and was confirmed by Owen and Gilbert.[3] The fact that in iron and iron–nickel alloys the product is metallographically distinguishable from martensite, but possesses the characteristics of a fairly constant transformation temperature over a range of cooling rates, strengthens the case for the shape change criterion as an identification of martensitic processes.

An interest in Owen's results, together with the contradictory values of M_s for pure iron obtained by extrapolation (Fe–Ni data extrapolate to 725°C at 0%Ni, while Fe–C data extrapolate to 520°C at 0%C), as well as the hope that a pure metal system would dispose of one variable, suggested an investigation of the martensitic transformation in pure iron. Towards the completion of our work, we were pleased to read that Yeo[6] had, as a result of his investigation of complex alloys based on Fe–Ni, suggested that 'carbon-free alloys should be studied for a reassessment of the theories of martensite formation'.

Previous measurements of M_s in pure iron have been made by Esser *et al.*,[7] Duwez,[8] Owen and Gilbert,[3] and Srivastava and Parr.[9] Table I summarizes the values of M_s obtained, the cooling rates at which a transformation described as martensitic occurred, and the purity of the iron. Two qualifications must be kept in mind, however, when the data in Table I are evaluated:

(i) the expressed composition of the iron is not inevitably correct. Carbon analyses at low values are not always reliable; the bar composition may not be typical of the sample used in the experiment, because of local segregation effects

(ii) there is no record of martensite formation being confirmed by metallographic examination for a shape change in any of the work quoted other than that of Srivastava and Parr.[9]

EXPERIMENTAL

Quenching experiments were conducted in an apparatus shown in Fig.1. Briefly, it consists of a tungsten wire heater surrounding the sample, which is suspended on chromel–alumel thermocouple wires, of 0·003in dia. This assembly is supported by a quartz fitting fastened to a cross-bar and pillar. Below the sample is a convergent–divergent nozzle designed to give supersonic gas velocities. A helium supply is controlled by a solenoid vacuum valve.

A small sample (usually about 0·005×0·01×0·01in) is heated to 1000°C and soaked for 5 min in a vacuum of 10^{-5} mm of mercury or better, and then quenched with helium gas by opening the solenoid valve. Cooling curves are obtained on an oscilloscope and recorded by a Polaroid Land camera.

In a subsidiary experiment an iron sample was contaminated with carbon, by heating the sample (in the unit) in a methane atmosphere maintained at 1in of mercury. After soaking for a time that depended upon the amount of carbon contamination required, the system was evacuated, and the sample transformed.

Two sources of iron were used: (*a*) Johnson Matthey spectrographic standard material: batch analysis shows 0·025%C; 0·0001%Si; 0·0005%Mn; 0·0003%Cu; 0·001% Ni; and less than 0·001% oxygen and nitrogen, and (*b*) iron supplied by the US Bureau of Mines, batch analysis shows 0·0015% metallic impurities and 0·0017% non-metallic impurities.

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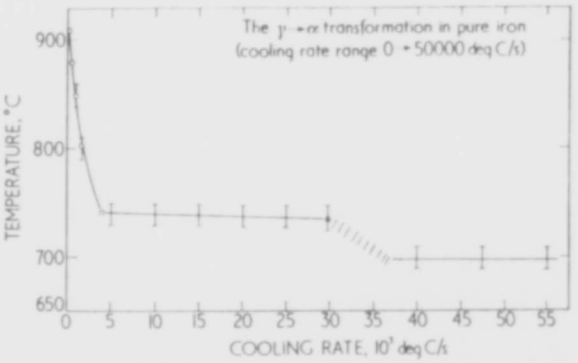
TABLE I M_s values obtained in various investigations

Investigation	Transformation temperature		Metal analysis, %	
	M_s, °C	Rate, degC/s		
Esser *et al.*	520	18000	carbon	0·017
			no record of metallics	
Gilbert and Owen	545	5500	C	0·010
			Si	0·005
			O_2	0·006
			S	0·004
			P	0·002
Duwez	750	12000	carbon	0·001
			trace metallic impurities	
			each less than	0·001
			O_2 less than	0·02
Srivastava and Parr	519	10000	C	0·005
			Si	0·02
			Ni	0·06



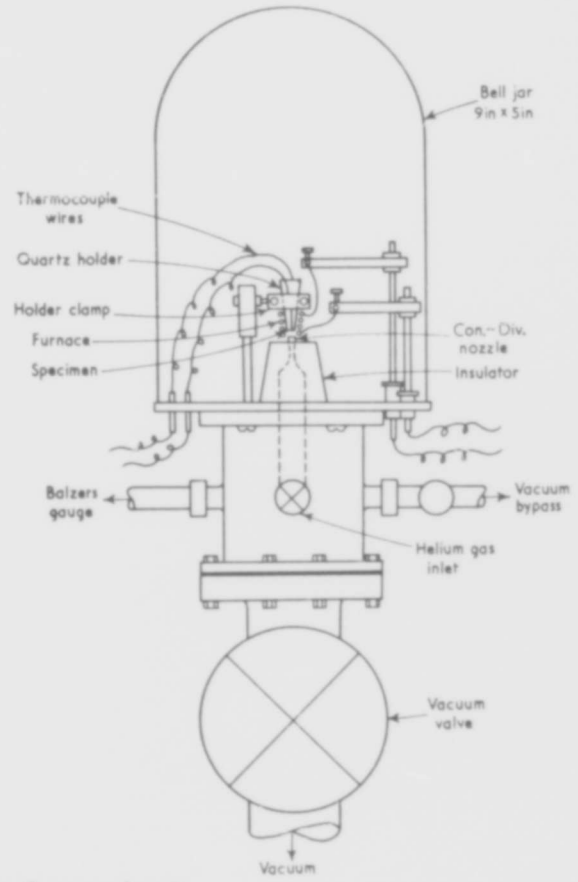
2 *The γ→α transformation in pure iron (cooling rate range 0–50000 degC/s)*

EXPERIMENTAL RESULTS

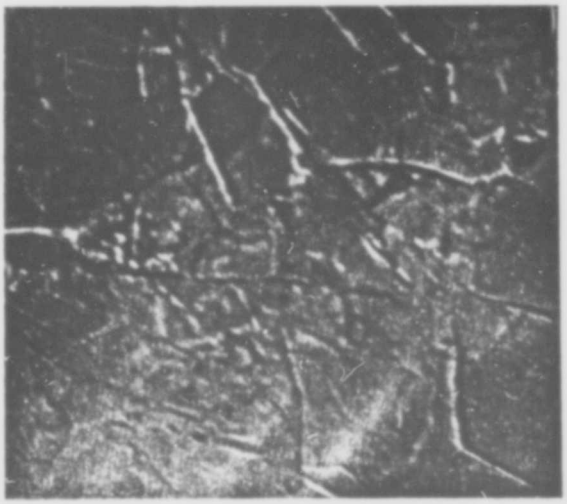
The results shown in Fig.2 represent the transformation temperature as a function of cooling rate for samples from source (*a*). Metallographic examination of samples polished before transformation showed surface rumpling when the lower transformation temperature (about 695°C) was measured (Fig.4). The higher transformation temperature (at cooling rates between 5000 and 30000 degC/s was associated with no surface rumpling (Fig.3). In Fig.5 the transformation temperature results (source (*a*) iron) at rates less than 10000 degC/s are compared with the figures of Duwez, and Gilbert and Owen.

During the course of the quenching experiments on source (*a*) iron, a number of samples were found to transform martensitically at the more frequently quoted M_s temperature, about 540°C, with appreciable scatter between 540° and 695°C. Experiments were conducted to determine whether this variation was attributable to prior thermal or mechanical history, but results were negative. The predominating feature was that any one sample always transformed at the same temperature for a given cooling rate, within an experimental error of less than ±5 degC. Microscopic examination of the iron bar stock showed what appeared to be small particles of cementite at some grain-boundary regions; it therefore seemed possible that, in view of the small size of our samples, this carbon heterogeneity might lead to samples containing different quantities of carbon. To test this assumption, a sample that transformed at 695°C at 40000 degC/s was subjected to an incremental carburizing treatment in natural gas, and subsequently after each treatment its transformation temperature was measured. The approximate amount of carbon absorbed by the specimen was assessed by measuring the Ac_3 temperature and assuming that, for a constant heating rate, Ac_3 would be lowered 10 degC/0·04%C. The measured M_s temperature dropped drastically with small carbon additions (Fig.6). Unfortunately, the actual carbon content of the iron that transforms martensitically at 700°C is not known accurately (for the analysis of such small samples was not possible).

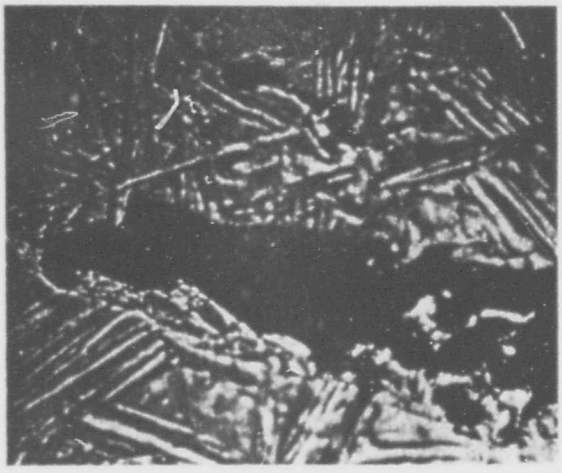
Iron from source (*b*) was obtained after most of our experiments with source (*a*) iron were completed. Samples transformed martensitically at 750°C (±5 degC). The critical rate for martensitic transformation was not measured,



1 *Gas quench unit*



3 *×750 massive equiaxed surface structure of iron cooled at 25000 degC/s. Transformation temperature 742°C*



4 *×750 martensite surface structure of iron cooled at 50000 degC/s. Transformation temperature 694°C*

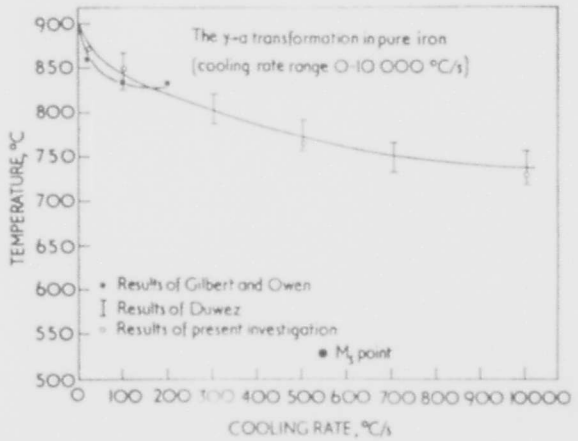
and the value of M_s quoted was obtained with a quenching rate of 52000 degC/s. The Ac_3 temperature of this iron was 916°C. The Ac_3 temperature of iron from source (*a*) whose M_s was 695°C, was 915°C (average of several samples). This implies that samples from source (*a*) that transformed martensitically at 695°C contained between 0·001% and 0·005 %C.

As the carbon content of the sample is increased, not only does the M_s temperature fall, but the critical quenching speed is reduced from 33000 degC/s for an M_s of 695°C, to 5000 degC/s for an M_s of 540°C.

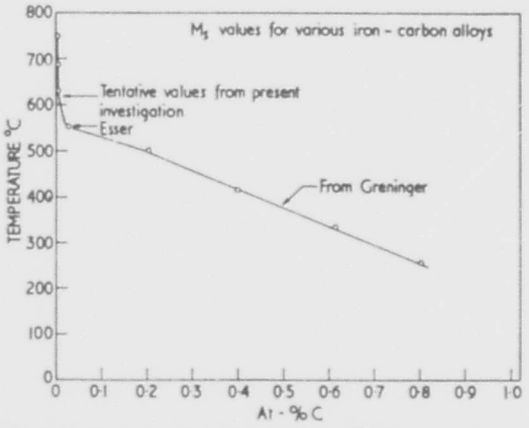
The effect of changing specimen size between 0·1in cube and 0·005×0·01×0·01in had no effect on transformation temperature at a given rate. Further, soaking temperatures between 950° and 1300°C had no effect. Hardness measurements made on transformed samples are summarized in Table II.

DISCUSSION

Taking our results in the context of earlier work, it is safe to assume that the 540°C transformation temperature is associated with carbon contents between about 0·005 and 0·01%. The scattered results reported by some workers and the spread we observed are to be expected if M_s *v.* carbon is as shown in Fig.6. The M_s temperature of our highest-purity material (source (*b*)), which contains less than



5 *The γ→α transformation in pure iron (cooling rate range 0–10000 degC/s)*



6 *M_s values for various iron–carbon alloys*

0·0017%C, is 750°C.* This temperature is sufficiently close to the quoted Curie temperature for iron (770°C) to remind one of Zener's[10] contention that fcc iron should transform to the bcc structure at the Curie temperature. However, we are not certain of the precise value of the Curie temperature for high-purity iron; and we are more intrigued by the approximate extrapolation of M_s at low carbon values to zero carbon, for it appears that M_s for pure iron (with substantially zero carbon) would lie between 800° and 900°C.

The M_s temperature for high-purity iron (source (b)) is in line with data extrapolated from Fe–Ni alloys. However, it appears that most, if not all, of the M_s data for such alloys pertained to massive rather than to martensitic transformations, which casts doubt on the value of these extrapolations. Recent work by Swanson,[11] however, yields an M_s value for iron extrapolated from Fe–Ni M_s data (the transformations were identified by shape change) of 680°C. The susceptibility of Fe–Ni alloys to carbon has been investigated by Yeo,[6] whose curve of M_s *v.* carbon content for an Fe–22·4%Ni alloy, has a pronounced upward turn at 0·02%C.

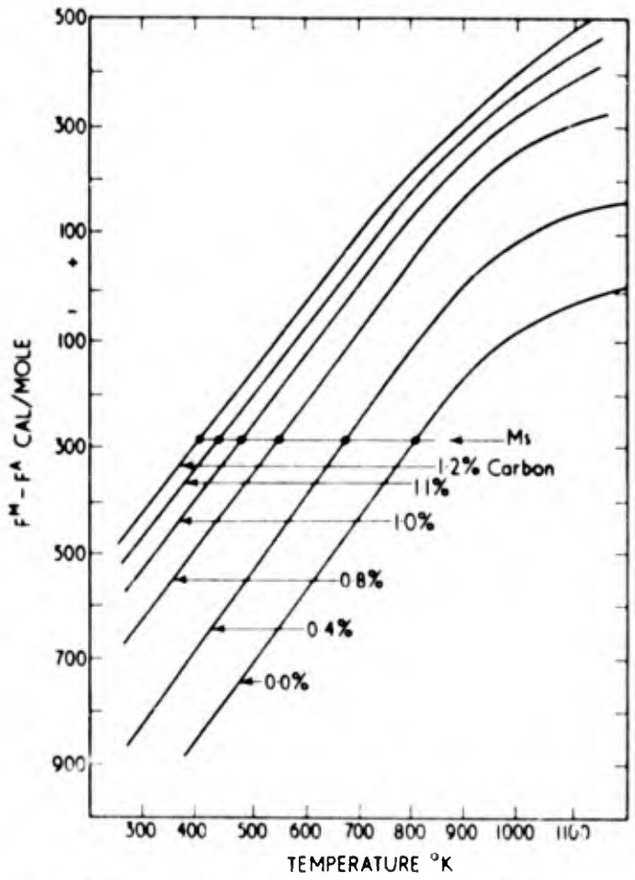
In the light of the newly established M_s temperature for pure iron, the thermodynamic approach[12] to the martensitic transformation is again cast into doubt. It has already been shown by Anderson and Hultgren[13] that the enthalpy data obtained by extrapolation involve an error that is of the same magnitude as the eventually calculated driving force of the austenite–martensite transformation. Further, Singh and Parr[14] have shown that an emf is generated by a cell

* After these tests, iron supplied by the Battelle Memorial Institute, containing 0·0009%C, gave confirmatory results.

TABLE II Microhardness results in pure iron

Heat treatment	Average microhardness, VPN	Remarks
1. Slowly cooled (100 degC/s)	112±15	average of 4 specimens: variation across any one sample ±10
2. Massive iron quenched at 25000 degC/s; transformation temperature 742°C	142±15	average of 3 specimens: variation across any one sample ±10
3. Quenched at 25000 degC/s; transformation temperature 525°C	164±25	Average of 3 specimens TT, °C* — Hardness, HV 1. 540 — 164±15 2. 525 — 154±10 3. 530 — 175±15
4. Quenched at 53000 degC/s	143±30	TT, °C* — hardness, HV 1. 695 — 136±10 2. 754 — 148±10

* Transformation temperature



7 *Free energy change accompanying the austenite–martensite transformation (after Cohen)*

whose electrodes are equiaxed ferrite and martensitic iron; this, in turn, demonstrates that the free energy of equiaxed ferrite is not the same as that of martensitic pure iron. Hence, an assumption that is implicit in the thermodynamic approach to martensitic transformations in Fe–C alloys[14] (i.e. that a strain-energy term is solely ascribable to tetragonality induced by carbon) appears to be in error.

However, accepting for the time being the general validity of the thermodynamic approach, a new anomaly occurs (Fig.7). The curves show the constancy of the free-energy difference between martensite (F^M) and austenite (F^A), regardless of carbon content, and imply that the driving force is always 290 cal/mole. However, if the M_s temperature for pure iron is not 540°C, but is in excess of 750°C, then, presumably, the driving force for the martensitic transformation in pure iron will be considerably reduced (to less than 100 cal/mole).

The effect of small carbon additions on M_s and the critical cooling rate may be rationalized by two possible hypotheses. The first relates to the interatomic forces induced by the insertion of carbon atoms into a periodic array of iron atoms. Very small deviations of iron atoms from their equilibrium positions involve large energy changes. A simple model implies that a sharp increase in the energy of the system will occur with the introduction of the first carbon atom, but a smaller increase occurs if the second carbon atom is placed sufficiently close to the first that the distortive effects of the first are present. Assuming that the effects of the first introduced carbon atom have a sphere of influence of ten atomic distances, the first carbon atom represents a weight concentration of about 0·005%. This figure, then, is the approximate amount of carbon up to which we would anticipate the greatest energy change in the system. Subsequent additions would have less effect. Therefore, if the martensitic transformation is to produce the bcc structure distorted by small quantities of carbon, we would expect an initial rapid depression of M_s up to about 0·005%C. An important criticism of this suggestion is that it assumes a uniform distribution of carbon atoms in interstitial positions, which is probably not the case.

The second hypothesis relates to the density of vacancies in γ iron. If a vacancy content of 1 in 10^4–10^5 is accepted, it is reasonable to suppose that initially added carbon atoms up to about 0·001% will reside in these sites in preference to interstitial sites. Smith's conclusions[15] that carbon atoms migrate to vacancy sites at 700°C offers some support. Thus the transformation requires less energy than it would were carbon atoms to be retained in the interstitial positions that become necessary at higher carbon levels. Further, we would expect the self-diffusion rate of iron to become substantially lower when vacancies are filled by carbon atoms, and interstitial sites taken up. Hence, at the critical carbon level at which M_s is substantially lowered, the cooling rate necessary to prevent the diffusion-controlled process $\gamma \rightarrow \alpha$ would be expected to become less. Therefore, if one subscribes to the view that the cooling rate for martensite production is determined by the necessity of preventing diffusion, the experimental results showing a simultaneous reduction of critical cooling rate and a depression of M_s are rationalized.

While the results presented do not constitute material for a new hypothesis of the general mechanisms of martensite formation, we feel that they cast sufficient doubt on the thermodynamic approach that other avenues should be re-explored. Philibert and Crussard[16] have tended towards a shock-wave model, which may be developed further. The solution of wave forms in a periodic lattice are of the type $\psi = A e^{i(wt - kna)}$ where: ψ=displacement; A=amplitude of the wave; w=frequency of the wave; a=lattice spacing; k=wave vector; t=time; n=1, 2, 3, etc.

Born and Huang[17] have shown that if k is complex, a resonant condition is set up in the lattice, which produces a vibration of infinite amplitude and hence lattice breakdown. Applying this to martensitic transformations, there may be a critical temperature (M_s) at which such behaviour occurs, as long as normal diffusion processes are suppressed. The theory is consistent with a number of characteristics of the martensitic process:

(i) martensitic growth occurs only when the lattice of the martensite plate is coherent with the parent phase, since the resonant wave will be stifled by a discontinuity. Thus the extent of growth will be controlled by the degree of registry of the martensitic and parent phases

(ii) the M_s temperature will be sensibly independent of cooling rate, as long as this is sufficient to prevent diffusion phenomena, since it is that temperature at which the proper wave-length spectrum is reached for resonance

(iii) since atomic vibrations are anisotropic, growth would be expected in preferred directions.

CONCLUSIONS

1. High-rate quenching experiments show that the M_s temperature in iron containing no more than 0·0017%C is 750°C.

2. M_s falls very rapidly with small additions of carbon to iron and M_s in pure iron would be expected to lie between 800° and 900°C.

3. The critical cooling rate necessary to produce martensite in iron containing less than about 0·005%C is at least 35000 degC/s. But the critical rate drops drastically with carbon additions. In iron containing sufficient carbon to show an M_s temperature of 540°C the critical rate is about 5000 degC/s.

4. The sharp change in behaviour of iron at a critical carbon content is tentatively rationalized on the basis of the effect of interstitial carbon atoms on bond energies, or by assuming vacancy sites for carbon atoms.

5. Since the thermodynamic approach to martensitic transformation theory is no longer consistent with the M_s temperature of 750°C in high-purity iron, and in view of the theory's other limitations, a suggestion is made which relates martensite formation to lattice resonance.

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REFERENCES

1. A. R. Troiano and A. B. Greninger: *Met. Prog.*, 1946, **50**, 303–307.
2. B. A. Bilby and J. W. Christian: *Inst. Metals*, Monograph and Report Series, 1956, **18**, 121.
3. W. S. Owen and A. Gilbert: *JISI*, 1960, **196**, 142–149.
4. A. Sauveur and C. H. Chou: *Trans. AIME*, 1929, **84**, 350–369.
5. T. B. Massalski: *Acta Met.*, 1958, **6**, 243–253.
6. R. B. G. Yeo: *Trans. AIME*, 1962, **224**, 1222.
7. H. Esser *et al.*: *Archiv Eisenh.*, 1933, **6**, 389–393.
8. P. Duwez: *Trans. AIME*, 1951, **191**, 765–771.
9. L. P. Srivastava and J. Gordon Parr: *Trans. AIME*, 1962, **224**, 1295.
10. C. Zener: 'Elasticity and Anelasticity', 37, 1952, University of Chicago Press.
11. W. D. Swanson and J. Gordon Parr: *JISI*, 1964, Feb., **202**, 104–106. [This issue].
12. M. Cohen *et al.*: 'Thermodynamics of Metallurgy', 242, 1952, ASM publication.
13. P. D. Anderson and H. Hultgren: *Trans. AIME*, 1962, **224**, 842.
14. K. P. Singh and J. Gordon Parr: *Acta Met.*, 1961, **9**, 1073–1074.
15. E. Smith: 'Direct observations of imperfections in crystals', 203, Wernick Editors, Met. Soc. AIME, Newkirk.
16. J. Philibert and C. Crussard: *JISI*, 1955, **180**, 39–50.
17. M. Born and K. Huang: 'Dynamical Theory of Crystal Lattices', 153, 1954, Oxford Clarendon Press.