

The prehistory of the phase rule, the steps taken by Gibbs and the crucial importance of the rule in understanding phase equilibria, are outlined in an article published in a German journal to mark its centenary (Petzow and Henig 1977).

One other scientist played a major role in establishing the examination of equilibrium diagrams – alternatively called phase diagrams – as a major part of the study of materials. This was Gustav Tammann (1861–1938), born to a German-speaking member of the Russian nobility (Figure 3.8). One of his several forenames was Apollon and indeed he attained something of the aura of the sun god himself. Tammann is a hero to German-speaking metallurgists (Köster 1939, 1961) and he is also regarded by some as a co-founder of the discipline of physical chemistry; he knew Arrhenius and van't Hoff well and interacted considerably with both; he knew Ostwald also but preferred to keep his distance: neither was a particularly easy man. He also came to know Roozeboom. As the biographical memoir by one of his descendants (Tammann 1970–1980) remarks, he first did research at the borders of chemistry and physics in 1883 when he began determining molecular weights from



Gustav Tammann (1861–1938)

Figure 3.8. Gustav Tammann.

the lowering of vapour pressures – and this was 4 years before Ostwald took up his chair in Leipzig. Influenced by Gibbs and Roozeboom, Tammann in his early base in Dorpat, in one of Russia's Baltic provinces (see Siilivask 1998) began in 1895 to study heterogeneous equilibria between liquid and vapour phases, and he also studied triple points. After some years, he reached the crucial conclusion (at variance with current opinion at the time) that all transitions from the crystalline state to other phases must be discontinuous, unlike the continuous liquid/vapour transition discovered by van der Waals. He published his researches leading to this conclusion in 1903.

A few years later he spent a time working with Nernst, before being invited in 1903 to occupy a newly established chair of inorganic chemistry in the University of Göttingen; when Nernst moved away from Göttingen in 1907, Tammann moved to his chair of physical chemistry and he held this until he retired in 1930. In Göttingen, Tammann worked with enormous energy (his biographer wrote that he was “a giant not only in stature but also in health and capacity for work; Tammann regularly worked in his laboratory for ten hours a day”) and he directed a large stable of research students who were also expected to keep long hours, and provoked notorious outbursts of rage when they failed to live up to expectation. He generated some 500 publications, highly unusual for a materials scientist, including successive editions of his famous *Lehrbuch der Metallographie*. Initially he worked mostly on inorganic glasses, in which field he made major contributions, before shifting progressively towards metals and alloys. He then began a long series of approximate studies of binary alloy systems, setting out to study alloys of 20 common metallic elements mixed in varying proportions in steps of 10 at.%, requiring 1900 alloys altogether. Using mainly thermal analysis and micrographic study, he was able to identify which proportions of particular metals formed proper intermetallic compounds, and established that the familiar valence relationships and stoichiometric laws applicable to salts do not at all apply to intermetallic compounds. From these studies he also reached the precocious hypothesis that some intermetallic compounds must have a non-random distribution of the atomic species on the lattice... and this before X-ray diffraction was discovered. This inspired guess was confirmed experimentally, by X-ray diffraction, in 1925, by Swedish physicists stimulated by Tammann's hypothesis. Tammann's very numerous alloy phase diagrams were of necessity rough and ready and cannot be compared with Heycock and Neville's few, but ultraprecise, phase diagrams.

Later, after the War, Tammann moved further towards physics by becoming interested in the mechanism of plastic deformation and the repair of deformed metals by the process of recrystallisation (following in the footsteps of Ewing and Rosenhain in Cambridge at the turn of the century), paving the way for the very extensive studies of these topics that followed soon after. Tammann thus followed

the dramatic shift of metallurgy away from chemical concerns towards physical aspects which had gathered momentum since 1900. In fact Tammann's chair was converted into a chair of physical metallurgy after his retirement, and this (after the next incumbent stepped down) eventually became a chair of metal physics.

The determination of equilibrium diagrams as a concern spread quite slowly at first, and it was only Tammann's extraordinary energy which made it a familiar concern. It took at least two decades after Roozeboom, and Heycock and Neville, at the turn of the century, to become widespread, but after that it became a central activity of metallurgists, ceramists and some kinds of chemists, sufficiently so that in 1936, as we shall see in Chapter 13, enough was known to permit the publication of a first handbook of binary metallic phase diagrams, and ternary diagrams followed in due course. In this slow start, the study of equilibrium diagrams resembled the determination of crystal structures after 1912.

As an indication of the central role that phase diagrams now play in the whole of materials science, the cumulative index for the whole of the 18-volume book series, *Materials Science and Technology* (Cahn *et al.* 1991–1998) can be cited in evidence. There are 89 entries under the heading “phase diagram”, one of the most extensive of all listings in this 390-page index.

3.1.2.1 Metastability. The emphasis in all of Gibbs's work, and in the students of phase diagrams who were inspired by him, was always on equilibrium conditions. A phase, or equilibrium, diagram denotes the phases (single or multiple), their compositions and ranges, stable for any alloy composition and any temperature. However, the long years of study of steels hardened by quenching into water, and the discovery in 1906 of age-hardening of aluminium alloys at room temperature, made it clear enough that the most interesting alloys are not in equilibrium, but find themselves, to coin a metaphor, in a state of suspended animation, waiting until conditions are right for them to approach true equilibrium at the temperature in question. This is possible because at sufficiently low temperatures, atomic movement (diffusion) in a crystalline material becomes so slow that all atoms are ‘frozen’ into their current positions. This kind of suspended animation is now seen to be a crucially important condition throughout materials science.

Wilhelm Ostwald was the first to recognise this state of affairs clearly. Indeed, he went further, and made an important distinction. In the second edition of his *Lehrbuch der Allgemeinen Chemie*, published in 1893, he introduced the concept of *metastability*, which he himself named. The simplest situation is just *instability*, which Ostwald likened to an inverted pyramid standing on its point. Once it begins to topple, it becomes ever more unstable until it has fallen on one of its sides, the new condition of stability. If, now, the tip is shaved off the pyramid, leaving a small flat

surface parallel to the base where the tip had been, and the pyramid is again carefully inverted, it will stand metastably on this small surface, and if it is very slightly tilted, will return to its starting position. Only a larger imposed tilt will now topple the pyramid. Thus, departing from the analogy, Ostwald pointed out that each state of a material corresponds to a definite (free) energy: an unstable state has a local maximum in free energy, and as soon as the state is “unfrozen”, it will slide down the free energy slope, so to speak. A metastable state, however, occupies a *local* minimum in free energy, and can remain there even if atomic mobility is reintroduced (typically, by warming); the state of true stability, which has a lower free energy, can only be attained by driving the state of the material over a neighbouring energy maximum. A water droplet supercooled below the thermodynamic freezing temperature is in metastable equilibrium so long as it is not cooled too far. A quenched aluminium alloy is initially in an unstable condition and, if the atoms can move, they form zones locally enriched in solute; such zones are then metastable against the nucleation of a transition phase which has a lower free energy than the starting state. Generally, whenever a process of *nucleation* is needed to create a more stable phase within a less stable phase, the latter can be maintained metastably; a tentative nucleus, or embryo, which is not large enough will redissolve and the metastable phase is locally restored. This is a very common situation in materials science.

The interpretation of metastable phases in terms of Gibbsian thermodynamics is set out simply in a paper by van den Broek and Dirks (1987).

3.1.2.2 Non-stoichiometry. One feature of phases that emerged clearly from the application of Gibbs's phase rule is that thermodynamics permit a phase to be not exactly stoichiometric; that is, a phase such as NiAl can depart from its ideal composition to, say, $\text{Ni}_{55}\text{Al}_{45}$ or $\text{Ni}_{45}\text{Al}_{55}$, without loss of its crystal structure; all that happens is that some atoms sit in locations meant for the other kind of atoms or, (in the special case of NiAl and a few other phases) some atomic sites remain vacant. The dawning recognition of the reality of non-stoichiometry, two centuries ago, convinced some chemists that atoms could not exist, otherwise, they supposed, strict stoichiometry would necessarily be enforced. One such sceptic was the famous French chemist Claude-Louis Berthollet (1748–1822); because of the observed non-stoichiometry of some compounds, he propounded a theory of *indefinite proportions* in chemical combination, which the work of John Dalton (1766–1844) and others succeeded in refuting, early in the nineteenth century. For a century, compounds with a wide composition range in equilibrium were known as *berthollides* while those of a very narrow range round the stoichiometric composition were known as *daltonides*. This terminology has now, rather regrettably, fallen out of use; one of the

last instances of its use was in a paper by the eminent Swedish crystallographer, Hägg (1950).

3.1.3 Microstructure

We come now to the third leg of the tripod, the third essential precursor of modern materials science. This is the study of microstructure in materials. When the practice of sectioning, polishing, etching and examining items such as steel ingots was first introduced, it was possible to see some features with the naked eye. Thus, Figure 3.9 shows the “macrostructure” of a cast ingot which has frozen rather slowly. The elongated, ‘columnar’ crystal grains stretching from the ingot surface into the interior can be clearly seen at actual (or even reduced) dimensions. But rapidly solidified metal has very fine grains which can only be seen under a microscope, as Henry Sorby came to recognise. The shape and size of grains in a single-phase metal or solid-solution alloy can thus fall within the province of either macro- or micro-structure.

At the turn of the century it was still widely believed that, while a metal in its ‘natural’ state is crystalline, after bending backwards and forwards (i.e., the process of fatigue damage), metal locally becomes amorphous (devoid of crystalline structure). Isolated observations (e.g., Percy 1864) showed that evidence of



Figure 3.9. Macrostructure in an ingot.

crystalline structure reappeared on heating, and it was thus supposed that the amorphous material re-crystallised. The man who first showed unambiguously that metals consist of small crystal grains was Walter Rosenhain (1875–1934), an engineer who in 1897 came from Australia to undertake research for his doctorate with an exceptional engineering professor, Alfred Ewing, at Cambridge. Ewing (1855–1935) had much broader interests than were common at the time, and was one of the early scientific students of ferromagnetism. He introduced the concept of hysteresis in connection with magnetic behaviour, and indeed coined the word. As professor of mechanism and applied mechanics at Cambridge University from 1890, he so effectively reformed engineering education that he reconciled traditionalists there to the presence of engineers on campus (Glazebrook 1932–1935), culminating in 1907 with the appointment of an engineer as permanent vice-chancellor (university president). Ewing may well have been the first engineering professor to study materials in their own right.

Ewing asked Rosenhain to find out how it was possible for a metal to undergo plastic deformation without losing its crystalline structure (which Ewing believed metals to have). Rosenhain began polishing sheets of a variety of metals, bending them slightly, and looking at them under a microscope. Figure 3.10 is an example of the kind of image he observed. This shows two things: plastic deformation entails displacement in shear along particular lattice planes, leaving 'slip bands', and those traces lie along different directions in neighboring regions... i.e., in neighboring crystal grains. The identification of these separate regions as distinct crystal grains was abetted by the fact that chemical attack produced crystallographic etch figures



Figure 3.10. Rosenhain's micrograph showing slip lines in lead grains.

of different shapes in the various regions. (Etching of polished metal sections duly became an art in its own right.) This work, published under the title *On the crystalline structure of metals* (Ewing and Rosenhain 1900), is one of the key publications in modern physical metallurgy. A byproduct of this piece of research, simple in approach but profound in implication, was the first clear recognition of recrystallisation after plastic deformation, which came soon after the work of 1900; it was shown that the boundaries between crystal grains can migrate at high temperatures. The very early observations on recrystallisation are summarised by Humphreys and Hatherly (1995).

It was ironic that a few years later, Rosenhain began to insist that the material inside the slip bands (i.e., between the layers of unaffected crystal) had become amorphous and that this accounted for the progressive hardening of metals as they were increasingly deformed: there was no instrument to test this hypothesis and so it was unfruitful, but none the less hotly defended!

In the first sentence of Ewing and Rosenhain's 1900 paper, the authors state that "The microscopic study of metals was initiated by Sorby, and has been pursued by Arnold, Behrens, Charpy, Chernoff, Howe, Martens, Osmond, Roberts-Austen, Sauveur, Stead, Wedding, Werth, and others". So, a range of British, French, German, Russian and American metallurgists had used the reflecting microscope (and Grignon in France in the 18th century had seen grains in iron even without benefit of a microscope, Smith 1960), but nevertheless it was not until 1900 that the crystalline nature of metals became unambiguously clear.

In the 1900 paper, there were also observations of deformation twinning in several metals such as cadmium. The authors referred to earlier observations in minerals by mineralogists of the German school; these had in fact also observed slip in non-metallic minerals, but that was not recognised by Ewing and Rosenhain. The repeated rediscovery of similar phenomena by scientists working with different categories of materials was a frequent feature of 19th-century research on materials.

As mentioned earlier, Heycock and Neville, at the same time as Ewing and Rosenhain were working on slip, pioneered the use of the metallurgical microscope to help in the determination of phase diagrams. In particular, the delineation of phase fields stable only at high temperatures, such as the β field in the Cu–Sn diagram (Figure 3.7) was made possible by the use of micrographs of alloys quenched from different temperatures, like those shown in Figure 3.11. The use of micrographs showing the identity, morphology and distribution of diverse phases in alloys and ceramic systems has continued ever since; after World War II this approach was immeasurably reinforced by the use of the electron microprobe to provide compositional analysis of individual phases in materials, with a resolution of a micrometre or so. An early text focused on the microstructure of steels was published by the American metallurgist Albert Sauveur (1863–1939), while an

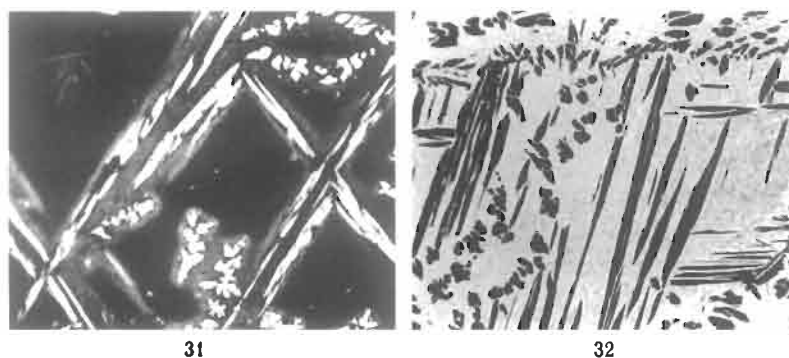


Figure 3.11. A selection of Heycock and Neville's micrographs of Cu-Sn alloys.

informative overview of the uses of microstructural examination in many branches of metallurgy, at a time before the electron microprobe was widely used, was published by Nutting and Baker (1965).

Ewing and Rosenhain pointed out that the shape of grains was initially determined simply by the chance collisions of separately nucleated crystallites growing in the melt. However, afterwards, when recrystallisation and grain growth began to be studied systematically, it was recognised that grain shapes by degrees approached metastable equilibrium – the ultimate equilibrium would be a single crystal, because any grain boundaries must raise the free energy. The notable English metallurgist Cyril Desch (1874–1958) (Desch 1919) first analysed the near-equilibrium shapes of metal grains in a polycrystal, and he made comparisons with the shapes of bubbles in a soapy water froth; but the proper topological analysis of grain shapes had to await the genius of Cyril Stanley Smith (1903–1992). His definitive work on this topic was published in 1952 and republished in fairly similar form, more accessibly, many years later (Smith 1952, 1981). Smith takes the comparison between metallic polycrystals and soap-bubble arrays under reduced air pressure further and demonstrates the similarity of form of grain-growth kinetics and bubble-growth kinetics. Grain boundaries are perceived as having an interface energy akin to the surface tension of soap films. He goes on to analyse in depth the topological relationships between numbers of faces, edges and corners of polyhedra in contact and the frequency distributions of polygonal faces with different numbers of edges as observed in metallic grains, biological cell assemblies and soap bubble arrays (Figure 3.12). This is an early example of a critical comparison between different categories of 'materials'. Cyril Smith was an exceptional man, whom we shall meet again in Chapter 14. Educated as a metallurgist in Birmingham University, he emigrated as a very young man to America where he became an industrial research metallurgist who published some key early papers on phase diagrams and phase

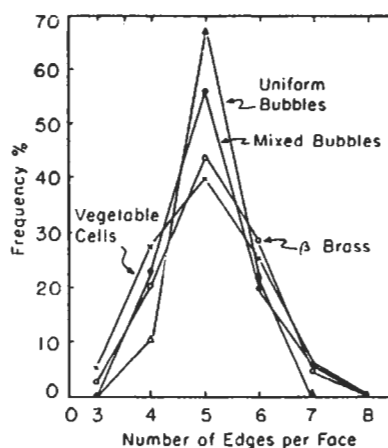


Figure 3.12. Frequency of various polygonal faces in grains, cells and bubbles (after C.S. Smith, *A Search for Structure*, 1981).

transformations, worked on the atom bomb at Los Alamos and then created the Institute for the Study of Metals at Chicago University (Section 14.4.1), before devoting himself wholly, at MIT, to the history of materials and to the relationship between the scientific and the artistic role of metals in particular. His books of 1960 and 1965 have already been mentioned.

The kind of quantitative shape comparisons published by Desch in 1919 and Smith in 1952 have since been taken much further and have given rise to a new science, first called quantitative metallography and later, *stereology*, which encompasses both materials science and anatomy. Using image analysers that apply computer software directly to micrographic images captured on computer screens, and working indifferently with single-phase and multiphase microstructures, quantities such as area fraction of phases, number density of particles, mean grain size and mean deviation of the distribution, mean free paths between phases, shape anisotropy, etc., can be determined together with an estimate of statistical reliability. A concise outline, with a listing of early texts, is by DeHoff (1986), while a more substantial recent overview is by Exner (1996). Figure 3.13, taken from Exner's treatment, shows examples of the ways in which quantities determined stereologically correlate with industrially important mechanical properties of materials. Stereology is further treated in Section 5.1.2.3.

A new technique, related to stereology, is *orientation-imaging*: here, the crystallographic orientations of a population of grains are determined and the misorientations between nearest neighbours are calculated and displayed graphically (Adams *et al.* 1993). Because properties of individual grain boundaries depend on

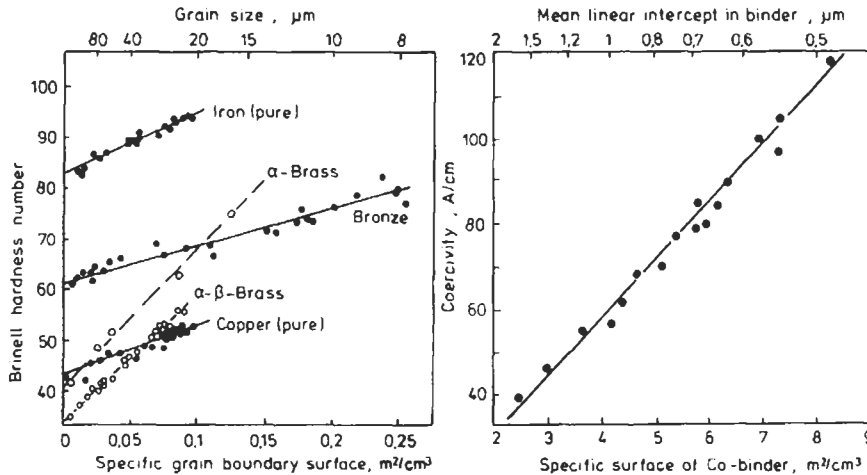


Figure 3.13. Simple relationships between properties and microstructural geometry: (a) hardness of some metals as a function of grain-boundary density; (b) coercivity of the cobalt phase in tungsten carbide/cobalt 'hard metals' as a function of interface density (after Exner 1996).

the magnitude and nature of the misorientation, such a grain-boundary character distribution (gbsd) is linked to a number of macroscopic properties, corrosion resistance in particular; the life of the lead skeleton in an automobile battery has for instance been greatly extended by controlling the gbsd.

The study of phase transformations, another crucial aspect of modern materials science, is intimately linked with the examination of microstructure. Such matters as the crystallographic orientation of interfaces between two phases, the mutual orientation of the two neighbouring phase fields, the nature of ledges at the interface, the locations where a new phase can be nucleated (e.g., grain boundaries or lines where three grains meet), are examples of features which enter the modern understanding of phase transformations. A historically important aspect of this is *age-hardening*. This is the process of progressive hardening of an unstable (quenched) alloy, originally one based on Al–Cu, during storage at room temperature or slightly above. It was accidentally discovered by Alfred Wilm in Germany during 1906–1909; it remained a total mystery for more than a decade, until an American group, Merica *et al.* (1920) demonstrated that the solubility of copper in solid aluminium decreases sharply with falling temperature, so that an alloy consisting of a *stable* solid solution when hot becomes supersaturated when it has been quenched to room temperature, but can only approach equilibrium very slowly because of the low mobility of the atoms in the solid. This very important paper in the history of physical metallurgy at once supplied a basis for finding other alloy systems capable of age-hardening, on the basis of known phase diagrams of binary alloys. In the words of the eminent

American metallurgist, R.F. Mehl, “no better example exists in metallurgy of the power of theory” (Mehl 1967). After this 1920 study, eminent metallurgists (e.g., Schmid and Wassermann 1928) struggled unsuccessfully, using X-rays and the optical microscope, to understand exactly what causes the hardening, puzzled by the fact that by the time the equilibrium phase, AlCu_2 , is visible in the microscope, the early hardening has gone again.

The next important stage in the story was the simultaneous and independent observation by Guinier (1938) in France and Preston (1938) in Scotland, by sophisticated X-ray diffraction analysis of *single crystals* of dilute Al–Cu alloy, that age-hardening was associated with “zones” enriched in copper that formed on $\{1\ 0\ 0\}$ planes of the supersaturated crystal. (Many years later, the “GP zones” were observed directly by electron microscopy, but in the 1930s the approach had to be more indirect.) A little later, it emerged that the microstructure of age-hardening alloys passes through several intermediate precipitate structures before the stable phase (AlCu_2) is finally achieved – hence the modern name for the process, *precipitation-hardening*. Microstructural analysis by electron microscopy played a crucial part in all this, and dislocation theory has made possible a quantitative explanation for the increase of hardness as precipitates evolve in these alloys. After Guinier and Preston’s pioneering research (published on successive pages of *Nature*), age-hardening in several other alloy systems was similarly analysed and a quarter century later, the field was largely researched out (Kelly and Nicholson 1963). One byproduct of all this was the recognition, by David Turnbull in America, that the whole process of age-hardening was only possible because the quenching process locked in a population of excess lattice vacancies, which greatly enhances atomic mobility. The entire story is very clearly summarised, with extracts from many classical papers, in a book by Martin (1968, 1998). It is worth emphasising here the fact that it was only when single crystals were used that it became possible to gain an understanding of the nature of age-hardening. Single crystals of metals are of no direct use in an industrial sense and so for many years no one thought of making them, but in the 1930s, their role in research began to blossom (Section 3.2.3 and Chapter 4, Section 4.2.1).

The sequence just outlined provides a salutary lesson in the nature of explanation in materials science. At first the process was a pure mystery. Then the relationship to the shape of the solid-solubility curve was uncovered; that was a *partial* explanation. Next it was found that the microstructural process that leads to age-hardening involves a succession of intermediate phases, none of them in equilibrium (a very common situation in materials science as we now know). An understanding of how these intermediate phases interact with dislocations was a further stage in explanation. Then came an understanding of the shape of the GP zones (planar in some alloys, globular in others). Next, the kinetics of the hardening needed to be

understood in terms of excess vacancies and various short-circuit paths for diffusion. The holy grail of complete understanding recedes further and further as understanding deepens (so perhaps the field is after all *not* researched out).

The study of microstructures in relation to important properties of metals and alloys, especially mechanical properties, continues apace. A good overview of current concerns can be found in a multiauthor volume published in Germany (Anon. 1981), and many chapters in my own book on physical metallurgy (Cahn 1965) are devoted to the same issues.

Microstructural investigation affects not only an understanding of structural (load-bearing) materials like aluminium alloys, but also that of functional materials such as 'electronic ceramics', superconducting ceramics and that of materials subject to irradiation damage. Grain boundaries, their shape, composition and crystallographic nature, feature again and again. We shall encounter these cases later on. Even alloys which were once examined in the guise of structural materials have, years later, come to fresh life as functional materials: a striking example is Al-4wt%Cu, which is currently used to evaporate extremely fine metallic conducting 'interconnects' on microcircuits. Under the influence of a flowing current, such interconnects suffer a process called electromigration, which leads to the formation of voids and protuberances that can eventually create open circuits and thereby destroy the operation of the microcircuit. This process is being intensely studied by methods which involve a detailed examination of microstructure by electron microscopy and this, in turn, has led to strategies for bypassing the problem (e.g., Shi and Greer 1997).

3.1.3.1 Seeing is believing. To conclude this section, a broader observation is in order. In materials science as in particle physics, *seeing is believing*. This deep truth has not yet received a proper analysis where materials science is concerned, but it has been well analysed in connection with particle (nuclear) physics. The key event here was C.T.R. Wilson's invention in 1911 (on the basis of his observations of natural clouds while mountain-climbing) of the "cloud chamber", in which a sudden expansion and cooling of saturated water vapour in air through which high-energy particles are simultaneously passing causes water droplets to nucleate on air molecules ionised by the passing particles, revealing particle tracks. To say that this had a stimulating effect on particle physics would be a gross understatement, and indeed it is probably no accident (as radical politicians like to say) that Wilson's first cloud-chamber photographs were published at about the same time as the atomic hypothesis finally convinced most of the hardline sceptics, most of whom would certainly have agreed with Marcellin Berthelot's protest in 1877: "Who has ever seen, I repeat, a gaseous molecule or an atom?"

A research student in the history of science (Chaloner 1997) recently published an analysis of the impact of Wilson's innovation under the title "The most wonderful experiment in the world: a history of the cloud chamber", and the professor of the history of science at Harvard almost simultaneously published a fuller account of the same episode and its profound implications for the sources of scientific belief (Galison 1997). Chaloner at the outset of his article cites the great Lord Rutherford: "It may be argued that this new method of Mr. Wilson's has in the main only confirmed the deductions of the properties of the radiations made by other more indirect methods. While this is of course in some respects true, I would emphasize the importance to science of the gain in confidence of the accuracy of these deductions that followed from the publication of his beautiful photographs." There were those philosophers who questioned the credibility of a 'dummy' track, but as Galison tells us, no less an expert than the theoretical physicist Max Born made it clear that "there is something deeply valued about the visual character of evidence".

The study of microstructural change by micrographic techniques, applied to materials, has similarly, again and again, led to a "gain in confidence". This is the major reason for the importance of microstructure in materials science. A further consideration, not altogether incidental, is that micrographs can be objects of great beauty. As Chaloner points out, Wilson's cloud-chamber photographs were of exceptional technical perfection...they were beautiful (as Rutherford asserted), more so than those made by his successors, and because of that, they were reproduced again and again and their public impact thus accumulated. A medical scientist quoted by Chaloner remarked: "Perhaps it is more an article of faith for the morphologist, than a matter of demonstrated fact, that an image which is sharp, coherent, orderly, fine textured and *generally aesthetically pleasing* is more likely to be true than one which is coarse, disorderly and indistinct". Aesthetics are a touchstone for many: the great theoretical physicists Dirac and Chandrasekhar have recorded their conviction that mathematical beauty is a test of truth – as indeed did an eminent pure mathematician, Hardy.

It is not, then, an altogether superficial observation that metallographers, those who use microscopes to study metals (and other kinds of materials more recently), engage in frequent public competitions to determine who has made the most beautiful and striking images. The most remarkable micrographs, like Wilson's cloud-chamber photographs, are reproduced again and again over the years. A fine example is Figure 3.14 which was made about 1955 and is still frequently shown. It shows a dislocation source (see Section 3.2.3.2) in a thin slice of silicon. The silicon was 'decorated' with a small amount of copper at the surface of the slice; copper diffuses fast in silicon and makes a beeline for the dislocation where it is held fast by the elastic stress field surrounding any

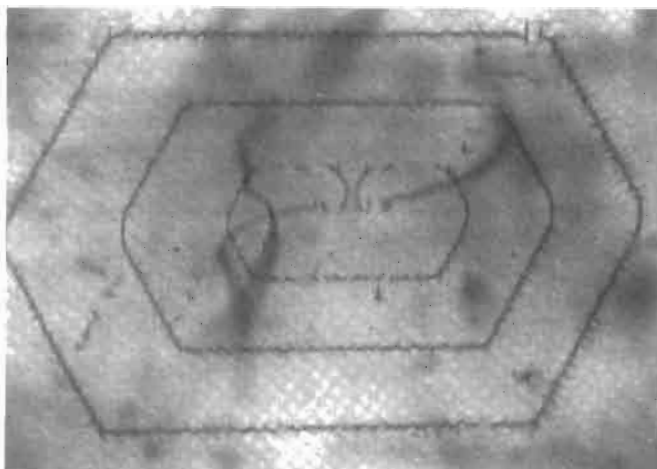


Figure 3.14. Optical micrograph of a dislocation source in silicon, decorated with copper (after W.C. Dash).

dislocation line. The sample has been photographed under a special microscope with optics transparent to infrared light; silicon is itself transparent to infrared, however, copper is not, and therefore the 'decorated' dislocation pattern shows up dark. This photograph was one of the very earliest direct observations of dislocations in a crystal; 'direct' here applies in the same sense in which it would apply to a track in one of Wilson's cloud-chambers. It is a ghost, but a very solid ghost.

3.2. SOME OTHER PRECURSORS

This chapter is entitled 'Precursors of Materials Science' and the foregoing major Sections have focused on the atomic hypothesis, crystallography, phase equilibria and microstructure, which I have presented as the main supports that made possible the emergence of modern materials science. In what follows, some other fields of study that made substantial contributions are more briefly discussed. It should be remembered that this is in no way a *textbook*; my task is not to explain the detailed nature of various phenomena and entities, but only to outline how they came to be invented or recognised and how they have contributed to the edifice of modern materials science. The reader may well think that I have paid too much attention, up to now, to metals; that was inevitable, but I shall do my best to redress the balance in due course.

3.2.1 Old-fashioned metallurgy and physical metallurgy

Until the late 19th century metallurgy, while an exceedingly flourishing technology and the absolute precondition of material civilization, was a craft and neither a science nor, properly speaking, a technology. It is not part of my task here to examine the details of the slow evolution of metallurgy into a proper science, but it is instructive to outline a very few stages along that road, from the first widely read texts on metallurgical practice (Biringuccio 1540, 1945, Agricola 1556, 1912). Biringuccio was really the first craftsman to set down on paper the essentials of what was experimentally known in the 16th century about the preparation and working of metals and alloys. To quote from Cyril Smith's excellent introduction to the modern translation: "Biringuccio's approach is largely experimental: that is, he is concerned with operations that had been found to work without much regard to why. The state of chemical knowledge at the time permitted no other sound approach. Though Biringuccio has a number of working hypotheses, he does not follow the alchemists in their blind acceptance of theory which leads them to discard experimental evidence if it does not conform." Or as Smith remarked later (Smith 1977): "Despite their deep interest in manipulated changes in matter, the alchemists' overwhelming trust in theory blinded them to facts". The mutual, two-way interplay between theory and experiment which is the hallmark of modern science comes much later.

The lack of any independent methods to test such properties as "purity" could lead Biringuccio into reporting error. Thus, on page 60 of the 1945 translation, he writes: "That metal (i.e., tin) is known to be purer that shows its whiteness more or... if when some part of it is bent or squeezed by the teeth it gives its natural cracking noise...". That cracking noise, we now know, is caused by the rapid creation of deformation twins. When, in 1954, I was writing a review paper on twinning, I made up some intentionally very impure tin and bit it: it crackled merrily.

Reverting to the path from Biringuccio and Agricola towards modern scientific metallurgy, Cyril Smith, whom we have already met and who was the modern master of metallurgical history (though, by his own confession (Smith 1981), totally untrained in history), has analysed in great detail the gradual realisation that steel, known for centuries and used for weapons and armour, was in essence an alloy of iron and carbon. As he explained (Smith 1981), up to the late 18th century there was a popular phlogiston-based theory of the constitution of steel: the idea was that iron was but a stage *in the reduction to the purest state, which was steel*, and it was only a series of painstaking chemical analyses by eminent French scientists which finally revealed that the normal form of steel was a *less* pure form of iron, containing carbon and manganese in particular (by the time the existence of these elements was recognised around the time of the French revolution). The metallurgical historian Wertime (1961), who has mapped out in great detail the development of steel

metallurgy and the understanding of the nature of steel, opines that “indeed, chemistry must in some degree attribute its very origins to iron and its makers”.

This is an occasion for another aside. For millenia, it was fervently believed by natural philosophers that purity was the test of quality and utility, as well as of virtue, and all religions, Judaism prominent among them, aspire to purity in all things. The anthropologist Mary Douglas wrote a famous text vividly entitled *Purity and Danger*; this was about the dangers associated with *impurity*. In a curious but intriguing recent book (Hoffmann and Schmidt 1997), the two authors (one a famous chemist, the other an expert on the Mosaic laws of Judaism) devote a chapter to the subtleties of “Pure/Impure”, prefacing it with an invocation by the prophet Jeremiah: “I have made you an assayer of My people – a refiner – You are to note and assay their ways. They are bronze and iron, they are all stubbornly defiant; they deal basely, all of them act corruptly.” Metallurgy is a difficult craft: the authors note that US President Herbert Hoover (the modern translator of Agricola), who was a connoisseur of critically minded people, opined that Jeremiah was a metallurgist “which might account for his critical tenor of mind”. The notion that *intentional* impurity (which is never called that – the name for it is ‘alloying’ or ‘doping’) is often highly beneficial took a very long time to be acceptable. Roald Hoffman, one of the authors of the above-mentioned book, heads one of his sections “Science and the Drive towards Impurity” and the reader quickly comes to appreciate the validity of the section title. So, a willing acceptance of intentional impurity is one of the hallmarks of modern materials science. However, all things go in cycles: once germanium and silicon began to be used as semiconductors, levels of purity never previously approached became indispensable, and before germanium or silicon could be usefully doped to make junctions and transistors, these metalloids had first to be ultrapurified. Purity necessarily precedes doping, or if you prefer, impurity comes before purity which leads to renewed impurity. That is today’s orthodoxy.

Some of the first stirrings of a scientific, experimental approach to the study of metals and alloys are fully analysed in an interesting history by Aitchison (1960), in which such episodes as Sorby’s precocious metallography and the discovery of age-hardening are gone into. Yet throughout the 19th century, and indeed later still, that scientific approach was habitually looked down upon by many of the most effective practical men. A good late example is a distinguished Englishman, Harry Brearley (1871–1948), who in 1913 invented (or should one say discovered?) stainless steel. He was very sceptical about the utility of ‘metallographists’, as scientific students of metals were known in his day. It is worth quoting *in extenso* what Brearley, undoubtedly a famous practical steelmaker, had to say in his (reissued) autobiography (Brearley 1995) about the conflict between the scientists and the practical men: “It would be foolish to deny the fruitfulness of the enormous labour, patient and often unrewarded, which has replaced the old cookery-book method of producing

alloyed metals by an understanding intelligence which can be called scientific. But it would be hardly less foolish to imagine, because a subject can be talked about more intelligibly, that the words invariably will be words of wisdom. The operations of an old trade may not lend themselves to complete representations by symbols, and it is a grievous mistake to suppose that what the University Faculty does not know cannot be worth knowing. Even a superficial observer might see that the simplifications, and elimination of interferences, which are possible and may be desirable in a laboratory experiment, may be by no means possible in an industrial process which the laboratory experiment aims to elucidate. To know the ingredients of a rice pudding and the appearance of a rice pudding when well made does not mean, dear reader, that you are able to make one." He went on to remark: "What a man sees through the microscope is more of less, and his vision has been known to be thereby so limited that he misses what he is looking for, which has been apparent at the first glance to the man whose eye is informed by experience." That view of things has never entirely died out.

At the same time as Brearley was discovering stainless steel and building up scepticism about the usefulness of metallographists, Walter Rosenhain, whom we have already met in Section 3.1.3 and who had quickly become the most influential metallurgist in Britain, was preparing to release a bombshell. In 1906 he had become the Superintendent of the Metallurgy Division of the new National Physical Laboratory at the edge of London and with his team of scientists was using a variety of physical methods to study the equilibria and properties of alloys. In 1913 he was writing his masterpiece, a book entitled *An Introduction to the Study of Physical Metallurgy*, which was published a year later (Rosenhain 1914). This book (which appeared in successive editions until 1934) recorded the transition of scientific metallurgy from being in effect a branch of applied chemistry to becoming an aspect of applied physics. It focused strongly on phase diagrams, a concept which emerged from physical-chemistry principles created by a mechanical engineer turned mathematical physicist. Gibbs single-handedly proved that in the presence of genius, scientific labels matter not at all, but most researchers are not geniuses.

Rosenhain (1917) published a book chapter entitled "The modern science of metals, pure and applied", in which he makes much of the New Metallurgy (which invariably rates capital letters!). In essence, this is an eloquent plea for the importance of basic research on metals; it is the diametric converse of the passage by Brearley which we met earlier.

In the three decades following the publication of Rosenhain's book, the physical science of metals and alloys developed rapidly, so that by 1948 it was possible for Robert Franklin Mehl (1898–1976) (see Smith 1990, Smith and Mullins 2001 and Figure 3.15), a doyen of American physical metallurgy, to bring out a book entitled *A Brief History of the Science of Metals* (Mehl 1948), which he then updated in the



Figure 3.15. Robert Franklin Mehl (courtesy Prof. W.W. Mullins).

historical chapter of the first edition of my multiauthor book, *Physical Metallurgy* (Cahn 1965). The 1948 version already had a bibliography of 364 books and papers. These masterly overviews by Mehl are valuable in revealing the outlook of his time, and for this purpose they can be supplemented by several critical essays he wrote towards the end of his career (Mehl 1960, 1967, 1975). After working with Sauveur at Harvard, Mehl in 1927, aged 29, joined the Naval Research Laboratory in Washington, DC, destined to become one of the world's great laboratories (see Rath and DeYoung 1998), as head of its brandnew Physical Metallurgy Division, which later became just the Metallurgy Division, indicating that 'physical metallurgy' and 'metallurgy' had become synonymous. So the initiative taken by Rosenhain in 1914 had institutional effects just a few years later. In Mehl's 1967 lecture at the Naval Research Laboratory (by this time he had been long established as a professor in Pittsburgh), he seeks to analyse the nature of physical metallurgy through a detailed

examination of the history of just one phenomenon, the decomposition (on heat-treatment) of austenite, the high-temperature form of iron and steel. He points out that “physical metallurgy is a very broad field”, and goes on later to make a fanciful comparison: “The US is a pluralistic nation, composed of many ethnic strains, and in this lies the strength of the country. Physical metallurgy is comparably pluralistic and has strength in this”. He goes on to assert something quite new in the history of metallurgy: “Theorists and experimentalists interplay. Someone has said that ‘no one believes experimental data except the man who takes them, but everyone believes the results of a theoretical analysis except the man who makes it’.” And at the end, having sucked his particular example dry, he concludes by asking “What is physical metallurgy?”, and further, how does it relate to the fundamental physics which in 1967 was well on the way to infiltrating metallurgy? He asks: “Is it not the primary task of metallurgists through research to *try to define a problem*, to do the initial scientific work, nowadays increasingly sophisticated, upon which the solid-state physicist can base his further and relentless probing towards ultimate causes?” That seems to me admirably to define the nature of the discipline which was the direct precursor of modern materials science. I shall rehearse further examples of the subject-matter of physical metallurgy later in this chapter, in the next two and in Chapter 9.

In 1932, Robert Mehl at the age of 34 became professor of metallurgy at Carnegie Institute of Technology in Pittsburgh, and there created the Metals Research Laboratory (Mehl 1975), which was one of *the* defining influences in creating the ‘new metallurgy’ in America. It is still, today, an outstanding laboratory. In spite of his immense positive influence, after the War Mehl dug in his heels against the materials science concept; it would be fair to say that he led the opposition. He also inveighed against vacancies and dislocations, which he thought tarred with the brush of the physicists whom he regarded as enemies of metallurgy; the consequences of this scepticism for his own distinguished experimental work on diffusion are outlined in Section 4.2.2. Mehl thought that metallurgy incorporated all the variety that was needed. According to a recently completed memoir (Smith and Mullins 2001), Mehl regarded “the move (to MSE) as a hollow gimmick to obtain funds...” Smith and Mullins go on to say “Nevertheless, he undoubtedly played a central and essential role in preparing the ground for the benefits of this broader view of materials”. So the foe of materials science inadvertently helped it on its way.

3.2.2 Polymorphism and phase transformations

In Section 3.1.1 we encountered the crystallographer and chemist Eilhardt Mitscherlich who around 1818 discovered the phenomenon of polymorphism in some substances, such as sulphur. This was the first recognition that a solid phase

can change its crystal structure as the temperature varies (a phase transformation), or alternatively that the same compound can crystallise (from the melt, the vapour or from a chemical reaction) in more than one crystalline form. This insight was first developed by the mineralogists (metallurgists followed much later). As a recent biography (Schütt 1997) makes clear, Mitscherlich started as an oriental linguist, began to study medicine and was finally sidetracked into chemistry, from where he learned enough mineralogy to study crystal symmetry, which finally led him to isomorphism and polymorphism.

The polymorphism of certain metals, iron the most important, was after centuries of study perceived to be the key to the hardening of steel. In the process of studying iron polymorphism, several decades were devoted to a red herring, as it proved: this was the β -iron controversy. β -iron was for a long time regarded as a phase distinct from α -iron (Smith 1965) but eventually found to be merely the ferromagnetic form of α -iron; thus the supposed transition from β to α -iron was simply the Curie temperature. β -iron has disappeared from the iron-carbon phase diagram and all transformations are between α and γ .

Polymorphism in nonmetals has also received a great deal of study and is particularly clearly discussed in a book by two Indian physicists (Verma and Krishna 1966) which also links to the phenomenon of polytypism, discussed in Section 3.2.3.4.

Of course, freezing of a liquid – or its inverse – are themselves phase transformations, but the scientific study of freezing and melting was not developed until well into the 20th century (Section 9.1.1). Polymorphism also links with metastability: thus aragonite, one polymorphic form of calcium carbonate, is under most circumstances metastable to the more familiar form, calcite.

The really interesting forms of phase transformations, however, are those where a single phase *precipitates* another, as in the age-hardening (= precipitation-hardening) process. Age-hardening is a good example of a *nucleation-and-growth* transformation, a very widespread category. These transformations have several quite distinct aspects which have been separately studied by different specialists – this kind of subdivision in the search for understanding has become a key feature of modern materials science. The aspects are: nucleation mechanism, growth mechanism, microstructural features of the end-state, crystallography of the end-state, and kinetics of the transformation process. Many transformations of this kind in both alloy and ceramic systems lead to a *Widmanstätten structure*, like that in Figure 3.4 but on a much finer scale. A beautiful example can be seen in Figure 3.16, taken from a book mentioned later in this paragraph. An early example of an intense study of one feature, the orientation relationship between parent and daughter phases, is the impressive body of crystallographic research carried out by C.S. Barrett and R.F. Mehl in Pittsburgh in the early 1930s, which led to the recognition that in

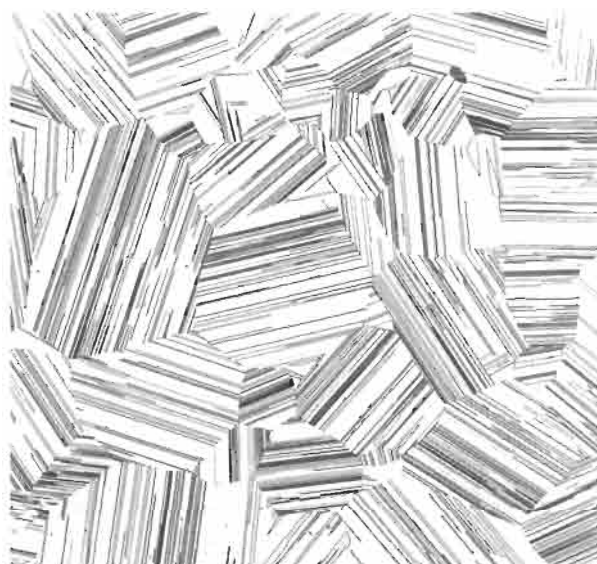


Figure 3.16. Widmanstätten precipitation of a hexagonal close-packed phase from a face-centred cubic phase in a Cu-Si alloy. Precipitation occurs on $\{111\}$ planes of the matrix, and a simple epitaxial crystallographic correspondence is maintained, $(0001)_{\text{hex}} \parallel (111)_{\text{cub}}$ (after Barrett and Massalski 1966).

transformations of this kind, plates are formed in such a way that the atomic fit at the interface is the best possible, and correspondingly the interface energy is minimised. This work, and an enormous amount of other early research, is concisely but very clearly reviewed in one of the classic books of physical metallurgy, *Structure of Metals* (Barrett and Massalski 1966). The underlying mechanisms are more fully examined in an excellent text mentioned earlier in this chapter (Porter and Easterling 1981), while the growth of understanding of age-hardening has been very clearly presented in a historical context by Martin (1968, 1998).

The historical setting of this important series of researches by Barrett and Mehl in the 1930s was analysed by Smith (1963), in the light of the general development of X-ray diffraction and single-crystal research in the 1920s and 1930s. The Barrett/Mehl work largely did without the use of single crystals and X-ray diffraction, and yet succeeded in obtaining many of the insights which normally required those approaches. The concept of *epitaxy*, orientation relationships between parent and daughter phases involved in phase transformations, had been familiar only to mineralogists when Barrett and Mehl began their work, but by its end, the concept had become familiar to metallurgists also and it soon became a favoured theme of

investigation. Mehl's laboratory in Pittsburgh in the 1930s was America's most prolific source of research metallurgists.

The kinetics of nucleation-and-growth phase transformations has proved of the greatest practical importance, because it governs the process of heat-treatment of alloys – steels in particular – in industrial practice. Such kinetics are formulated where possible in terms of the distinct processes of nucleation rates and growth rates, and the former have again to be subdivided according as nuclei form all at once or progressively, and according as they form homogeneously or are restricted to sites such as grain boundaries. The analysis of this problem – as has so often happened in the history of materials science – has been reinvented again and again by investigators who did not know of earlier (or simultaneous) research. Equations of the general form $f = 1 - \exp(-kt^n)$ were developed by Gustav Tammann of Göttingen (Tammann 1898), in America by Melvin Avrami (who confused the record by changing his name soon after) and by Johnson and the above-mentioned Mehl both in 1939, and again by Ulick Evans of Cambridge (Evans 1945), this last under the title “The laws of expanding circles and spheres in relation to the lateral growth of surface films and the grain size of metals”. There is a suggestion that Evans was moved to his investigation by an interest in the growth of lichens on rocks. A.N. Kolmogorov, in 1938, was another of the pioneers.

The kinetics of diffusion-controlled phase transformations has long been a focus of research and it is vital information for industrial practice as well as being a fascinating theme in fundamental physical metallurgy. An early overview of the subject is by Aaronson *et al.* (1978).

A quite different type of phase transformation is the *martensitic* type, named by the French metallurgist Floris Osmond after the German 19th-century metallographer Adolf Martens. Whereas the nucleation-and-growth type of transformation involves migration of atoms by diffusive jumps (Section 4.2.2) and is often very slow, martensitic transformations, sometimes termed diffusionless, involve regimented shear of large groups of atoms. The hardening of carbon-steel by quenching from the γ -phase (austenite) stable at high temperatures involves a martensitic transformation. The crystallographic relationships involved in such transformations are much more complex than those in nucleation-and-growth transformations and their elucidation is one of the triumphs of modern transformation theory. Full details can be found in the undisputed bible of phase transformation theory (Christian 1965). Georgi Kurdjumov, the Russian ‘father of martensite’, appears in Chapter 14.

There are other intermediate kinds of transformations, such as the bainitic and massive transformations, but going into details would take us too far here. However, a word should be said about *order–disorder transformations*, which have played a major role in modern physical metallurgy (Barrett and Massalski 1966). Figure 3.17 shows the most-studied example of this, in the Cu–Au system: the nature of the

process shown here was first identified in Sweden in 1925, where there was a flourishing school of “X-ray metallographers” in the 1920s (Johansson and Linde 1925). At high temperatures the two kinds of atom are distributed at random (or nearly at random) over all lattice sites, but on cooling they redistribute themselves on groups of sites which now become crystallographically quite distinct. Many alloys behave in this way, and in the 1930s it was recognised that the explanation was based on the Gibbsian competition between internal energy and entropy: at high temperature entropy wins and disorder prevails, while at low temperatures the stronger bonds between unlike atom pairs win. This picture was quantified by a simple application of statistical mechanics, perhaps the first application to a phase transformation, in a celebrated paper by Bragg and Williams (1934). (Bragg’s recollection of this work in old age can be found in Bragg (1975, 1992), p. 212.) The ideas formulated here are equally applicable to the temperature-dependent alignment of magnetic spins in a ferromagnet and to the alignment of long organic molecules in a liquid crystal. Both the experimental study of order–disorder transitions (in some of them, very complex microstructures appear, Tanner and Leamy 1974) and the theoretical convolutions have attracted a great deal of attention, and ordered alloys, nowadays called *intermetallics*, have become important structural materials for use at high temperatures. The complicated way in which order–disorder transformations fit midway between physical metallurgy and solid-state physics has been surveyed by Cahn (1994, 1998).

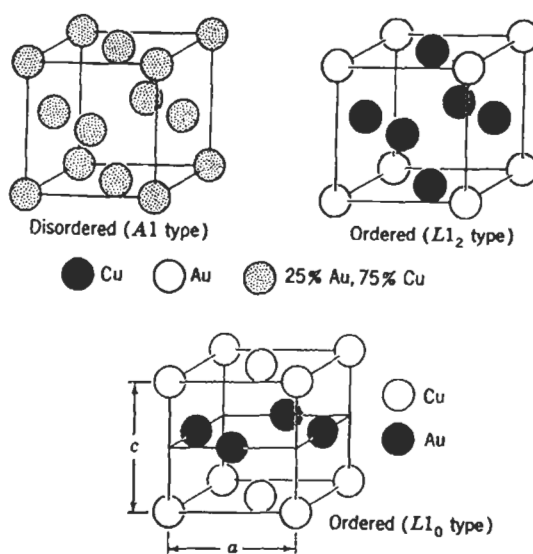


Figure 3.17. Ordering in Cu–Au alloys.

The Bragg–Williams calculation was introduced to metallurgical undergraduates (this was before materials science was taught as such) for the first time in a pioneering textbook by Cottrell (1948), based on his teaching in the Metallurgy Department at Birmingham University, England; Bragg–Williams was combined with the Gibbsian thermodynamics underlying phase diagrams, electron theory of metals and alloys and its applications, and the elements of crystal defects. This book marked a watershed in the way physical metallurgy was taught to undergraduates, and had a long-lasting influence.

The whole field of phase transformations has rapidly become a favourite stamping-ground for solid-state physicists, and has broadened out into the closely related aspects of phase stability and the prediction of crystal structures from first theoretical principles (e.g., de Fontaine 1979, Stocks and Gonis 1989). Even professional mathematicians are moving into the game (Gurtin 1984). The extremely extensive and varied research on phase transformations by mainline materials scientists is recorded in a series of substantial conference proceedings, with a distinct emphasis on microstructural studies (the first in the series: Aaronson *et al.* 1982); a much slimmer volume that gives a good sense of the kind of research done in the broad field of phase transformations is the record of a symposium in honor of John Kirkaldy, a nuclear physicist turned materials scientist (Embury and Purdy 1988); his own wide-ranging contribution to the symposium, on the novel concept of ‘thermologistics’, is an illustration of the power of the phase-transformation concept! A good example of a treatment of the whole field of phase transformations (including solidification) in a manner which represents the interests of mainline materials scientists while doing full justice to the physicists’ extensive input is a multiauthor book edited by Haasen (1991).

While most of the earlier research was done on metals and alloys, more recently a good deal of emphasis has been placed on ceramics and other inorganic compounds, especially ‘functional’ materials used for their electrical, magnetic or optical properties. A very recent collection of papers on oxides (Boulesteix 1998) illustrates this shift neatly. In the world of polymers, the concepts of phase transformations or phase equilibria do not play such a major role; I return to this in Chapter 8.

The conceptual gap between metallurgists (and nowadays materials scientists) on the one hand and theoretical solid-state physicists and mathematicians on the other, is constantly being bridged (Section 3.3.1) and as constantly being reopened as ever new concepts and treatments come into play in the field of phase transformations; the large domain of critical phenomena, incorporating such recondite concepts as the renormalisation group, is an example. There are academic departments, for instance one of Materials Science at the California Institute of Technology, which are having success in bridging conceptual gaps of this kind.

3.2.2.1 Nucleation and spinodal decomposition. One specific aspect of phase transformations has been so influential among physical metallurgists, and also more recently among polymer physicists, that it deserves a specific summary; this is the study of the nucleation and of the spinodal decomposition of phases. The notion of homogeneous nucleation of one phase in another (e.g., of a solid in a supercooled melt) goes back all the way to Gibbs. Minute embryos of different sizes (that is, transient nuclei) constantly form and vanish; when the product phase has a lower free energy than the original phase, as is the case when the latter is supercooled, then some embryos will survive if they reach a size large enough for the gain in volume free energy to outweigh the energy that has to be found to create the sharp interface between the two phases. Einstein himself (1910) examined the theory of this process with regard to the nucleation of liquid droplets in a vapour phase. Then, after a long period of dormancy, the theory of nucleation kinetics was revived in Germany by Max Volmer and A. Weber (1926) and improved further by two German theoretical physicists of note, Richard Becker and Wolfgang Döring (1935). (We shall meet Volmer again as one of the key influences on Frank's theory of crystal growth in 1953, Section 3.2.3.3.) Reliable experimental measurements became possible much later still in 1950, when David Turnbull, at GE, perfected the technique of dividing a melt up into tiny hermetic compartments so that heterogeneous nucleation catalysts were confined to just a few of these; his measurements (Turnbull and Cech 1950, Turnbull 1952) are still frequently cited.

It took a long time for students of phase transformations to understand clearly that there exists an alternative way for a new phase to emerge by a diffusive process from a parent phase. This process is what the Nobel-prize-winning Dutch physicist Johannes van der Waals (1837–1923), in his doctoral thesis, first christened the “spinodal”. He recognised that a liquid beyond its liquid/gas critical point, having a negative compressibility, was unstable towards *continuous changes*. A negative Gibbs free energy has a similar effect, but this took a very long time to become clear. The matter was at last attacked head-on in a famous theoretical paper (based on a 1956 doctoral thesis) by the Swedish metallurgist Mats Hillert (1961): he studied theoretically both atomic segregation and atomic ordering, two alternative diffusional processes, in an unstable metallic solid solution. The issue was taken further by John Cahn and the late John Hilliard in a series of celebrated papers which has caused them to be regarded as the creators of the modern theory of spinodal decomposition; first (Cahn and Hilliard 1958) they revived the concept of a *diffuse* interface which gradually thickens as the unstable parent phase decomposes *continuously* into regions of diverging composition (but, typically, of similar crystal structure); later, John Cahn (1961) generalised the theory to three dimensions. It then emerged that a very clear example of spinodal decomposition in the solid state had been studied in detail as long ago as 1943, at the Cavendish by Daniel and

Lipson (1943, 1944), who had examined a copper–nickel–iron ternary alloy. A few years ago, on an occasion in honour of Mats Hillert, Cahn (1991) mapped out in masterly fashion the history of the spinodal concept and its establishment as a widespread alternative mechanism to classical nucleation in phase transformations, specially of the solid–solid variety. An excellent, up-to-date account of the present status of the theory of spinodal decomposition and its relation to experiment and to other branches of physics is by Binder (1991). The Hillert/Cahn/Hilliard theory has also proved particularly useful to modern polymer physicists concerned with structure control in polymer blends, since that theory was first applied to these materials in 1979 (see outline by Kyu 1993).

3.2.3 *Crystal defects*

I treat here the principal types of point defects, line defects, and just one of the many kinds of two-dimensional defects. A good, concise overview of all the many types of crystal defects, and their effects on physical and mechanical properties, has been published by Fowler *et al.* (1996).

3.2.3.1 Point defects. Up to now, the emphasis has been mostly on metallurgy and physical metallurgists. That was where many of the modern concepts in the physics of materials started. However, it would be quite wrong to equate *modern* materials science with physical metallurgy. For instance, the gradual clarification of the nature of point defects in crystals (an essential counterpart of dislocations, or line defects, to be discussed later) came entirely from the concentrated study of ionic crystals, and the study of polymeric materials after the Second World War began to broaden from being an exclusively chemical pursuit to becoming one of the most fascinating topics of physics research. And that is leaving entirely to one side the huge field of semiconductor physics, dealt with briefly in Chapter 7. Polymers were introduced in Chapter 2, Section 2.1.3, and are further discussed in Chapter 8; here we focus on ionic crystals.

At the beginning of the century, nobody knew that a small proportion of atoms in a crystal are routinely missing, even less that this was not a matter of accident but of thermodynamic equilibrium. The recognition in the 1920s that such “vacancies” had to exist in equilibrium was due to a school of statistical thermodynamicians such as the Russian Frenkel and the Germans Jost, Wagner and Schottky. That, moreover, as we know now, is only one kind of “point defect”; an atom removed for whatever reason from its lattice site can be inserted into a small gap in the crystal structure, and then it becomes an “interstitial”. Moreover, in insulating crystals a point defect is apt to be associated with a local excess or deficiency of electrons,

producing what came to be called “colour centres”, and this can lead to a strong sensitivity to light: an extreme example of this is the photographic reaction in silver halides. In all kinds of crystal, pairs of vacancies can group into divacancies and they can also become attached to solute atoms; interstitials likewise can be grouped. All this was in the future when research on point defects began in earnest in the 1920s.

At about the same time as the thermodynamicians came to understand why vacancies had to exist in equilibrium, another group of physicists began a systematic experimental assault on colour centres in insulating crystals: this work was mostly done in Germany, and especially in the famous physics laboratory of Robert Pohl (1884–1976) in Göttingen. A splendid, very detailed account of the slow, faltering approach to a systematic knowledge of the behaviour of these centres has recently been published by Teichmann and Szymborski (1992), as part of a magnificent collaborative history of solid-state physics. Pohl was a resolute empiricist, and resisted what he regarded as premature attempts by theorists to make sense of his findings. Essentially, his school examined, patiently and systematically, the wavelengths of the optical absorption peaks in synthetic alkali halides to which controlled “dopants” had been added. (Another approach was to heat crystals in a vapour of, for instance, an alkali metal.) Work with X-ray irradiation was done also, starting with a precocious series of experiments by Wilhelm Röntgen in the early years of the century; he published an overview in 1921. Other physicists in Germany ignored Pohl’s work for many years, or ridiculed it as “semiphysics” because of the impurities which they thought were bound to vitiate the findings. Several decades were yet to elapse before minor dopants came to the forefront of applied physics in the world of semiconductor devices. Insofar as Pohl permitted any speculation as to the nature of his ‘colour centres’, he opined that they were of non-localised character, and the adherents of localised and of diffuse colour centres quarrelled fiercely for some years. Even without a theoretical model, Pohl’s cultivation of optical spectroscopy, with its extreme sensitivity to minor impurities, led through collaborations to advances in other fields, for instance, the isolation of vitamin D.

One of the first experimental physicists to work with Pohl on impure ionic crystals was a Hungarian, Zoltan Gyulai (1887–1968). He rediscovered colour centres created by X-ray irradiation while working in Göttingen in 1926, and also studied the effect of plastic deformation on the electrical conductivity. Pohl was much impressed by his Hungarian collaborator’s qualities, as reported in a little survey of physics in Budapest (Radnai and Kunfalvi 1988). This book reveals the astonishing flowering of Hungarian physics during the past century, including the physics of materials, but many of the greatest Hungarian physicists (people like Szilard, Wigner, von Neumann, von Karman, Gabor, von Hevesy, Kurti (who has just died at age 90 as I write this), Teller (still alive)) made their names abroad because the unceasing sequence of revolutions and tyrannies made life at home too

uncomfortable or even dangerous. However, Gyulai was one of those who returned and he later presided over the influential Roland Eötvös Physical Society in Budapest.

Attempts at a theory of what Pohl's group was discovering started in Russia, whose physicists (notably Yakov Frenkel and Lev Landau) were more interested in Pohl's research than were most of his own compatriots. Frenkel, Landau and Rudolf Peierls, in the early 1930s, favoured the idea of an electron trapped "by an extremely distorted part of the lattice" which developed into the idea of an "exciton", an activated atom. Finally, in 1934, Walter Schottky in Germany first proposed that colour centres involved a pairing between an anion vacancy and an extra (trapped) electron – now sometimes called a "Schottky defect". (Schottky was a rogue academic who did not like teaching and migrated to industry, where he fastened his teeth on copper oxide rectifiers; thus he approached a fundamental problem in alkali halides via an industrial problem, an unusual sequence at that time.)

At this point, German research with its Russian topdressing was further fertilised by sudden and major input from Britain and especially from the US. In 1937, at the instigation of Nevill Mott (1905–1996) (Figure 3.18), a physics conference was held in Bristol University, England, on colour centres (the beginning of a long series of influential physics conferences there, dealing with a variety of topics including also dislocations, crystal growth and polymer physics). Pohl delivered a major experimental lecture while R.W. Gurney and Mott produced a quantum theory of colour centres, leading on soon afterwards to their celebrated model of the photographic effect. (This sequence of events was outlined later by Mitchell 1980.)

The leading spirit in the US was Frederick Seitz (b. 1911) (Figure 3.19). He first made his name with his model, jointly with his thesis adviser, Eugene Wigner, for calculating the electron band structure of a simple metal, sodium. Soon afterwards he spent two years working at the General Electric Company's central research centre (the first and at that time the most impressive of the large industrial laboratories in America), and became involved in research on suitable phosphorescent materials ("phosphors") for use as a coating in cathode-ray tubes; to help him in this quest, he began to study Pohl's papers. (These, and other stages in Seitz's life are covered in some autobiographical notes published by the Royal Society (Seitz 1980) and more recently in an autobiographical book (Seitz 1994).) Conversations with Mott then focused his attention on crystal defects. Many of the people who were to create the theory of colour centres after the War devoted themselves meanwhile to the improvement of phosphors for radar (TV tubes were still in the future), before switching to the related topic of radiation damage in relation to the Manhattan Project. After the War, Seitz returned to the problem of colour centres and in 1946 published the first of two celebrated reviews (Seitz 1946), based on his resolute attempts to unravel the nature of colour centres. Theory was now buttressed by



Figure 3.18. Nevill Francis Mott (courtesy Mrs. Joan Fitch).

purpose-designed experiments. Otto Stern (with two collaborators) was able to show that when ionic crystals had been greatly darkened by irradiation and so were full of colour centres, there was a measurable decrease in density, by only one part in 10^4 . (This remarkably sensitive measurement of density was achieved by the use of a flotation column, filled with liquid arranged to have a slight gradient of density from top to bottom, and establishing where the crystal came to rest.) Correspondingly, the concentration of vacancies in metals was measured directly by an equally ingenious experimental approach due to Feder and Nowick (1958), followed up later by Simmons and Balluffi (1960–1963): they compared dilatometry (measurements of changes in length as a function of changing temperature) with precision measurements of lattice parameter, to extract the concentration of vacancies in equilibrium at various temperatures. This approach has proved very fruitful.

Vacancies had at last come of age. Following an intense period of research at the heart of which stood Seitz, he published a second review on colour centres (Seitz 1954). In this review, he distinguished between 12 different types of colour centres, involving single, paired or triple vacancies; many of these later proved to be



Figure 3.19. Frederick Seitz (courtesy Dr. Seitz).

misidentifications, but nevertheless, in the words of Teichmann and Szyzborski, “it was to Seitz’s credit that, starting in the late 1940s, both experimental and theoretical efforts became more convergent and directed to the solution of clearly defined problems”. The symbiosis of quantitative theory and experiment (which will be treated in more detail in Chapter 5) got under way at much the same time for metals and for nonmetals.

Nowick (1996) has outlined the researches done on crystal defects during the period 1949–1959 and called this the “golden age of crystal defects”. A recent, very substantial overview (Kraftmakher 1998) admirably surveys the linkage between vacancies in equilibrium and ‘thermophysical’ properties of metals: this paper includes a historical table of 32 key papers, on a wide range of themes and techniques, 1926–1992.

Point defects are involved in many modern subfields of materials science: we shall encounter them again particularly in connection with diffusion (Chapter 4, Section 4.2.2) and radiation damage (Chapter 5, Section 5.1.3).

3.2.3.2 Line defects: dislocations. The invention of dislocations is perhaps the most striking example in the history of materials science of a concept being recognised as soon as the time is ripe. A dislocation is a *line defect*, in a crystal, which is linked to an elastic stress field within a crystal in such a way that under an external stress, a dislocation is impelled to move through the crystal and thereby causes a permanent change of shape... i.e., plastic deformation. Dislocations were invented – that is the right word, they were *not* initially ‘discovered’ – mainly because of a huge mismatch between the stress calculated from first principles for the stress needed to deform crystal plastically, and the much smaller stress actually observed to suffice. A subsidiary consideration which led to the same explanatory concept was the observation that any crystalline material subjected to plastic deformation thereby becomes harder – it *work-hardens*. Three scientists reached the same conclusion at almost the same time, and all published their ideas in 1934: Michael Polanyi (1891–1976), Geoffrey Taylor (1886–1975), both of them already encountered, and Egon Orowan (1902–1989): two of these were emigré Hungarians, which shows again the remarkable contributions to science made by those born in this country of brilliant scholars, of whom so many were forced by 20th-century politics into emigration.

The papers which introduced the concept of a dislocation all appeared in 1934 (Polanyi 1934, Taylor 1934, Orowan 1934). Figure 3.20 shows Orowan’s original sketch of an edge dislocation and Taylor’s schematic picture of a dislocation moving. It was known to all three of the co-inventors that plastic deformation took place by slip on lattice planes subjected to a higher shear stress than any of the other symmetrically equivalent planes (see Chapter 4, Section 4.2.1). Taylor and his collaborator Quinney had also undertaken some quite remarkably precise calorimetric research to determine how much of the work done to deform a piece of metal

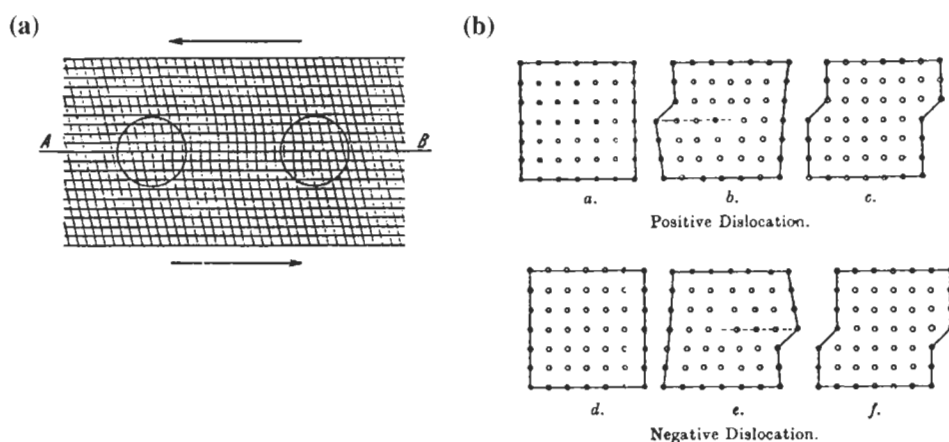


Figure 3.20. An edge dislocation, as delineated by Orowan (a) and Taylor (b).

remained behind as stored energy, and Taylor decided that this stored energy must be localised as elastic distortion at some kind of crystal defect; he also believed that work-hardening must be due to the interaction between these defects, which increased in concentration by some unknown mechanism. Orowan was also intrigued by the fact that some of his zinc crystals when stressed deformed in a discontinuous, jerky fashion (he reflected about this observation all his life, as many great scientists tend to do about their key observations) and decided that each 'jerk' must be due to the operation of one defect. All three were further moved by the recognition that plastic deformation begins at stresses very much lower (by a factor of ≈ 1000) than would be necessary if the whole slip plane operated at once. The defects illustrated in Figure 3.20 can move under quite small stresses, in effect because only a small area of slip plane glides at any one instant. In the 3 papers, this is presented as the result of a local elastic enhancement of stress, but it is in fact more accurate to present the matter as a reduction in the stress needed to move the defect. Taylor, alone, used his theory to interpret the actual process of work-hardening, and he was no doubt driven to this by consideration of his own measurements of the measured retained energy of cold work (Taylor and Quinney 1934).

The above very abbreviated account of the complicated thought processes that led Polanyi, Taylor and Orowan to their simultaneous papers can be expanded by reference to detailed accounts, including autobiographical notes by all three. One interesting fact that emerges from Polanyi's own account (Polanyi 1962) is that his paper was actually ready several months before Orowan's, but he was already in regular contact with Orowan and, learning that Orowan's ideas were also rapidly gelling, Polanyi voluntarily waited and submitted his paper at the same time as Orowan's, and they appeared side by side in the same issue of *Zeitschrift für Physik*. Polanyi was a gentleman of the old school; his concern with ethics was no doubt one of the impulses which drove him later in life to become a professional philosopher; he dropped crystal plasticity after 1934. The movement of Taylor's ideas can be found in a recent biography (Batchelor 1996). This includes a passage contributed by Nevill Mott and another by Taylor himself. At the end of this passage, Taylor points out that when he had finished the work on crystal plasticity, he went back promptly to his beloved fluid mechanics and to the design of novel anchors (he was an enthusiastic yachtsman). Nevertheless, over the years Taylor did a great deal of work on the mechanics of monocrystals and polycrystals, on the calorimetric determination of retained energy of cold work (he took several bites at this hard cherry) and on the nature of work-hardening: his 41 papers in this broad area have been collected in one impressive volume (Batchelor 1958). However, dislocations featured very little in these papers.

Only Orowan remained with the topic and contributed a number of seminal ideas to the theory of the interaction between moving dislocations and other dislocations

or other obstacles inside a crystal. In an excellent biographical memoir of Orowan (Nabarro and Argon 1995) we learn Orowan's side of things. He confirms Polanyi's self-denying decision; he is quoted as writing: "...slowly I recognised that dislocations were important enough to warrant a publication, and I wrote to Polanyi, with whom I discussed them several times, suggesting a joint paper. He replied that it was my bird and I should publish it; finally we agreed that we would send separate papers to Professor Scheel, editor of the *Zeitschrift für Physik*, and ask him to print them side by side. This he did." He also expressed, 50 years after the event, his sceptical reaction to Taylor's version; indeed he went so far as to say in a letter to one of the memoirists that "his theory was no theory at all"! In the memoir, among many other fascinating things, we learn how Orowan escaped from the practice of electrical engineering which his father sought to impose upon him (to ensure that his son could earn a living). Orowan was at Göttingen University and, in between designing transformers, he proposed to spend one day a week in an advanced physics laboratory. In late 1928 he visited Professor Richard Becker (a highly influential solid-state physicist whom we shall meet again) to get an enrollment card signed. In Orowan's own words, recorded in the memoir, "my life was changed by the circumstance that the professor's office was a tremendously large room... Becker was a shy and hesitating man; but by the time I approached the door of the huge room he struggled through with his decision making, called me back and asked whether I would be interested in checking experimentally a 'little theory of plasticity' he (had) worked out three years before. Plasticity was a prosaic and even humiliating proposition in the age of de Broglie, Heisenberg and Schrödinger, but it was better than computing my sixtieth transformer, and I accepted with pleasure. I informed my father that I had changed back to physics; he received the news with stoic resignation." In fact, by another trivial accident (a fellow student asked a challenging question) he worked for his doctorate not on plasticity but on cleavage of mica! The work that led to the dislocation came afterwards. On such small accidents can a researcher's lifetime work depend.

After 1934, research on dislocations moved very slowly, and little had been done by the time the War came. After the War, again, research at first moved slowly. In my view, it was not coincidence that theoretical work on dislocations accelerated at about the same time that the first experimental demonstrations of the actual existence of dislocations were published and turned 'invention' into 'discovery'. In accord with my remarks in Section 3.1.3, it was a case of 'seeing is believing'; all the numerous experimental demonstrations involved the use of a microscope. The first demonstration was my own observation, first published in 1947, of the process of polygonization, stimulated and christened by Orowan (my thesis adviser). When a metal crystal is plastically bent, it is geometrically necessary that it contains an excess of positive over negative dislocations; when the crystal is then heated, most of the dislocations of

opposite signs 'climb' and demolish one another, but the excess dislocations remain behind and arrange themselves into stable walls of subgrain-boundaries, which can be revealed by suitable etching. Elastic theory quickly proved that such walls would actually be the most stable configuration for an array of dislocations of the same sign. The detailed story of the discovery of polygonization has been told (Cahn 1985). At Bell Laboratories, Vogel *et al.* (1953) took my observation a notch further and proved, using germanium crystals, that the density of etchpits along a small-angle subgrain-boundary exactly matched the density of dislocations needed to produce the measured angular misorientation along the boundary.

Following this, there was a rapid sequence of observations: J.W. Mitchell in Bristol 'decorated' networks of dislocations in silver chloride by irradiating the crystals with ultraviolet light to nucleate minute silver crystals at favoured sites, viz., dislocation lines. He has given a circumstantial account of the sequence of events that led to this indirect method of observing dislocation geometries (Mitchell 1980). We have already seen Dash's method of revealing dislocations in silicon by 'decorating' them with copper (Figure 3.14). Another group (Gilman and Johnston) at General Electric were able to reveal successive positions of dislocations in lithium fluoride by repeated etching; at the place where a dislocation line reaches the surface, etching generates a sharp-bottomed etchpit, a place where it previously surfaced and was etched but where it is no longer located turns into a blunt-bottomed etchpit. This technique played a major part in determining how the speed of moving dislocations related to the magnitude of applied stress. All these microscopic techniques of revealing dislocation lines were surveyed in masterly fashion by an expert microscopist (Amelinckx 1964). A much more recent survey of the direct observation of dislocations has been provided by Braun (1992) as part of his account of the history of the understanding of the mechanical properties of solids.

The 'clincher' was the work of Peter Hirsch and his group at the Cavendish Laboratory in 1956. A transmission electron microscope was acquired by this group in 1954; the next year images were seen in deformed aluminium foils which Michael Whelan suspected to reveal dislocation lines (because the lattice nearby is distorted and so the Bragg reflection of the electron beam is diverted to slightly different angles). Once both imaging and local-area diffraction from the same field of view became possible, in mid-1956, the first convincing images of moving dislocations were obtained – more than 20 years after the original publication of the dislocation hypothesis. The history of this very important series of researches is systematically told by Hirsch (1986) and is outlined here in Section 6.2.2.1. Nevill Mott has told of his delight when "his young men burst into his office" and implored him to come and see a moving dislocation, and Geoffrey Taylor also, working in Cambridge at the time on quite different matters, was highly pleased to see his hypothesis so elegantly vindicated.

One of the big problems initially was to understand how the relatively few dislocations that are grown into crystals can multiply during plastic deformation, increasing their concentration by a factor of more than thousandfold. The accepted answer today is the Frank–Read source, of which Figure 3.14 is a specimen. The segment of dislocation line between two powerful pinning points (constituted by other dislocations skew to the plane of the source) moves rapidly under stress, emits a complete dislocation ring and returns to its initial geometry to start over again. Charles Frank (1911–1998) has recorded in brief and pithy form how this configuration acquired its name (Frank 1980). He and his co-originator, Thornton Read (W.T. Read, Jr.), who worked at Bell Laboratories, in 1950 were introduced to each other in a hotel in Pittsburgh, just after Frank had given a lecture at Cornell University and conceived the source configuration. Frank was told at the hotel that Read had something to tell him; it was exactly the same idea. On checking, they found that they had their brainwaves within an hour of each other two days previously. So their host remarked: “There is only one solution to that, you must write a joint paper”, which is what they did (Frank and Read 1950). Coincidence rarely comes more coincident than this!

Mott played a major part, with his collaborator Frank Nabarro (b. 1917) and in consultation with Orowan, in working out the dynamics of dislocations in stressed crystals. A particularly important early paper was by Mott and Nabarro (1941), on the flow stress of a crystal hardened by solid solution or a coherent precipitate, followed by other key papers by Koehler (1941) and by Seitz and Read (1941). Nabarro has published a lively sequential account of their collaboration in the early days (Nabarro 1980). Nabarro originated many of the important concepts in dislocation theory, such as the idea that the contribution of grain boundaries to the flow stress is inversely proportional to the square root of the grain diameter, which was later experimentally confirmed by Norman Petch and Eric Hall.

The early understanding of the geometry and dynamics of dislocations, as well as a detailed discussion of the role of vacancies in diffusion, is to be found in one of the early classics on crystal defects, a hard-to-find book entitled *Imperfections in Nearly Perfect Crystals*, based on a symposium held in the USA in 1950 (Shockley *et al.* 1952).³ Since in 1950, experimental evidence of dislocations was as yet very sparse, more emphasis was placed on a close study of slip lines (W.T. Read, Jr.,

³ The Shockley involved in this symposium was the same William Shockley who had participated in the invention of the transistor in 1947. Soon after that momentous event, he became very frustrated at Bell Laboratories (and virtually broke with his coinventors, Walter Brattain and John Bardeen), as depicted in detail in a rivetting history of the transistor (Riordan and Hoddeson 1997). For some years, while still working at Bell Laboratories, he became closely involved with dislocation geometry, clearly as a means of escaping from his career frustrations, before eventually turning fulltime to transistor manufacture.

p. 129), following in Ewing and Rosenhain's footsteps. Orowan did not participate in this symposium, but his detailed reflections on dislocation dynamics appeared two years later in another compilation (Koehler *et al.* 1954). The first systematic account of the elastic theory of dislocations, based to a considerable degree on his own work, was published by Cottrell (1953). This book has had a lasting influence and is still frequently cited. In Chapter 5, I shall reexamine his approach to these matters.

Dislocations are involved in various important aspects of materials apart from mechanical behaviour, such as semiconducting behaviour and crystal growth. I turn next to a brief examination of crystal growth.

3.2.3.3 Crystal growth. As we saw in the preceding section, before World War II the dislocation pioneers came to the concept through the enormous disparity between calculated and measured elastic limiting stresses that led to plastic deformation. The same kind of disparity again led to another remarkable leap of imagination in post-war materials science.

Charles Frank (1911–1998; Figure 3.21), a physicist born in South Africa, joined the productive physics department at Bristol University, in England, headed by Nevill Mott, soon after the War. According to Braun's interview with Frank (Braun 1992), Mott asked Frank to lecture on crystal growth (a subject of which at first he knew little) and Frank based himself upon a textbook published in Germany just before the War, which a friend had sent him as a 'postwar present' (Frank 1985). This book, by the physical chemist Max Volmer (1939), was about the kinetics of phase transformations, and devoted a good deal of space to discussing the concept of *nucleation*, a topic on which Volmer had contributed one of the key papers of the interwar years (Volmer and Weber 1926). We have already met this crucial topic in Section 3.2.2.1; suffice it to say here that the point at issue is the obstacle to creating the first small 'blob' of a stable phase within a volume of a phase which has been rendered metastable by cooling or by supersaturation (in the case of a solution). I avowedly use the term 'metastable' here rather than 'unstable': random thermal fluctuations generate minute 'embryos' of varying sizes, but unless these exceed a critical size they cannot survive and thus redissolve, and that is the essence of metastability. The physical reason behind this is the energy needed to create the interface between the embryo of the stable phase and the bulk of the metastable phase, and the effect of this looms the larger, the smaller the embryo. The theory of this kind of 'homogeneous' nucleation, also known as the 'classical theory', dates back to Volmer and Weber (see a survey by Kelton 1991).

While Charles Frank was soaking up Volmer's ideas in 1947, Volmer himself was languishing as a slave scientist in Stalin's Russia, as described in a recent book about

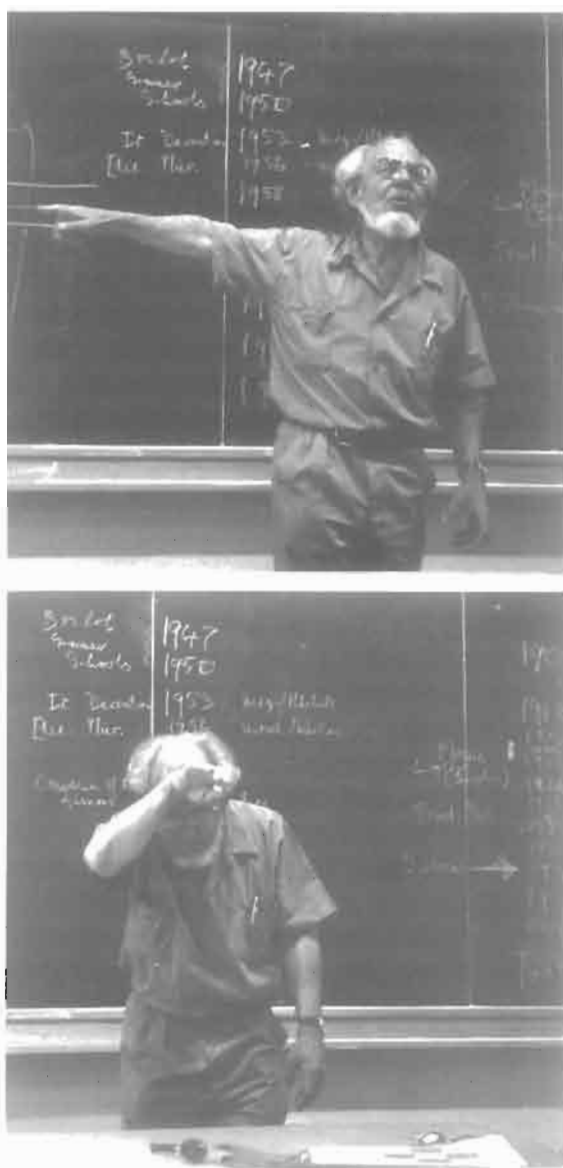


Figure 3.21. Charles Frank (courtesy Prof. J.-P. Poirier).

the Soviet race for the atom bomb (Riehl and Seitz 1996); so Frank could not consult him. Instead he argued with his roommates, N. Cabrera and J. Burton. Volmer in his book had described the growth of iodine crystals from the vapour at just 1%

supersaturation, and Burton and Cabrera, stimulated by the argumentative Frank, calculated what supersaturation would be needed for a *perfect* (defect-free) iodine crystal to continue to grow, using methods based on Volmer's work and on another key German paper by Becker and Döring (1935) devoted to two-dimensional nucleation, and they concluded that a supersaturation of 50% would be necessary. The point here is that a deposited iodine atom skittering across the crystal surface would readily attach itself to a ledge, one atom high, of a growing layer (a small supersaturation would suffice for this), but once the layer is complete, an incoming atom then needs to join up with several others to form a stable nucleus, and do so before it re-evaporates. Only at a very high supersaturation would enough iodine atoms hit the surface, close together in space and time, to form a viable nucleus quickly enough.

At the same time as Burton and Cabrera were making their calculation, Frank Nabarro, who was to become a high priest of dislocations in his later career, drew Frank's attention to the (postulated) existence of screw dislocations. These differ from the edge dislocations sketched in Figure 3.20, because the (Burgers) vector that determines the quantum of shear displacement when a dislocation passes a point in a crystal is now not normal to the dislocation line, as in Figure 3.20, but parallel to it, as in Figure 3.22. In a flash of inspiration, Frank realized that this kind of defect provides an answer to the mismatch between theory and experiment pinpointed by Burton, because the growing layer can never be complete: as the layer rotates around the dislocation axis, there is always a step to which arriving iodine atoms can attach themselves.

Burton and Cabrera explained their calculations at the famed 1949 Faraday Discussion on Crystal Growth in Bristol (Faraday Society 1949, 1959a), and Frank

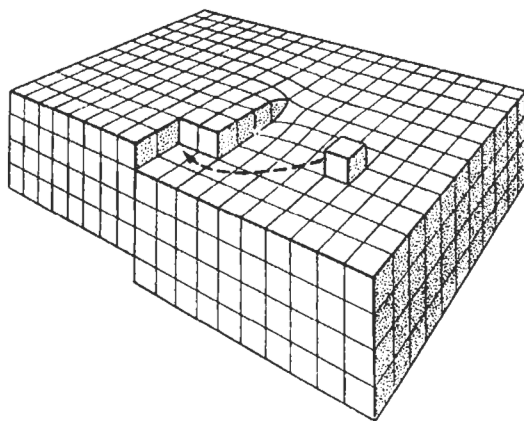


Figure 3.22. Screw dislocation and crystal growth, after W.T. Read.

described his dislocation model; he had only developed it days before the conference opened. The three together set out the whole story briefly in *Nature* in 1949 and in extenso in a famous and much-cited paper (Burton *et al.* 1951). Volmer was of course unable to attend the Faraday Society Discussion, but Richard Becker was there and contributed a theoretical paper. Thus Becker had a double link with dislocations: in 1928 he gave Orowan the opportunity that led to his 1934 paper, and he coauthored a paper that helped lead Burton, Cabrera and Frank to the inspiration that they revealed in Bristol in 1949 and developed fully by 1951.

Frank's model implies as an unavoidable corollary that the growing surface takes the form of a spiral; each rotation of the growing step mounts on the previous rotations which also keep on growing. Nobody had, apparently, reported such spirals, until a young mineralogist working in another physics department, L.J. Griffin, at another Bristol conference later in 1949 tried to attract Frank's attention, at first without success: when at last he succeeded, Griffin showed Frank beautiful growth spirals on a surface of a crystal of the mineral beryl, revealed by phase contrast microscopy (which can detect step heights very much smaller than a wavelength of light). Braun (1992) tells the entire story of the Bristol crystal growth theory, on the basis of an interview with Frank, and remarks that the effect of Griffin's revelation "was shattering...The pictures were shown to all and aroused great excitement". I was there and can confirm the excitement. Once Griffin's pictures had been publicised, all sorts of other microscopists saw growth spirals within months on all kinds of other crystals. It was a fine illustration of the fact that observers often do not see what is staring them in the face until they know exactly what they are looking for.

What is really important about the events of 1934 and 1949 is that on each occasion, theoretical innovation was driven directly by a massive mismatch between measurement and old theory. The implications of this are examined in Chapter 5.

Frank's prediction of spiral growth on crystal surfaces, followed by its successful confirmation, had an indirect but major effect on another aspect of modern science. In his 1968 book, *The Double Helix: A Personal Account of the Discovery of the Structure of DNA*, Watson (1968) describes how, not long before the final confirmation of the helical structure of DNA, he and Crick were arguing whether tobacco mosaic virus (TMV) has a helical structure; Crick was sceptical. Watson wrote: "My morale automatically went down, until I hit upon a foolproof reason why subunits should be helically arranged. In a moment of after-supper boredom I had read a Faraday Society Discussion on 'The Structure of Metals' (he remembered wrong: it was actually devoted to Crystal Growth). It contained an ingenious theory by the theoretician F.C. Frank on how crystals grow. Every time the calculations were properly done, the paradoxical answer emerged that the crystals could not grow at anywhere near the observed rates. Frank saw that the paradox vanished if crystals

were not as regular as suspected, but contained dislocations resulting in the perpetual presence of cosy corners into which new molecules could fit. Several days later...the notion came to me that each TMV particle should be thought of as a tiny crystal growing like other crystals through the possession of cosy corners. Most important, the simplest way to generate cosy corners was to have the subunits helically arranged. The idea was so simple that it had to be right." Crick remained sceptical for the time being, but the seed that led to the double helix was firmly sown in Watson's mind.

3.2.3.4 Polytypism. Just after Frank and his colleagues had announced their triumph, in 1950, a young Indian physicist, Ajit Ram Verma, was awarded a fellowship to undertake research in the laboratory of a noted microscopist, S. Tolansky, in London University. Tolansky was experienced in detecting minute steps at surfaces, of the order of single atom height, by two methods: phase-contrast microscopy (as used by Griffin, one of his students) and multiple beam interferometry, a subtle technique which produces very narrow and sharp interference fringes that show small discontinuities where there is a surface step. In the immediate aftermath of the Bristol innovations, Tolansky asked Verma to concentrate on studying crystal surfaces; Verma had brought a variety of crystals with him from India, and some of these were of silicon carbide, SiC, as he explains in an autobiographical essay (Verma 1982). He now set out to look for growth spirals. Using ordinary optical microscopy he was successful in observing his first spirals by simply breathing on the surface; as he later recognised, water drops condensed preferentially at the ledges of the spiral, and rendered the very low steps visible; thus, one form of nucleation was called into service to study another form of nucleation. Then, using phase contrast and multiple-beam interferometry to measure step heights, he published his first growth spirals on silicon carbide in *Nature*, only to find that the adjacent paper on the same page, by Severin Amelinckx in Belgium (Verma and Amelinckx, 1951), showed exactly the same thing (Figure 3.23). Both measured the step height and found that it matched the unit cell height, as it should. (This episode is reminiscent of the adjacent but entirely independent publication of Letters to *Nature* concerning the mechanism of age-hardening, by Guinier and by Preston, in 1938.)

On silicon carbide, it is easier to see and measure step heights than in crystals like beryl, because SiC has *polytypes*, first discovered by the German crystallographer Baumhauer (1912). The crystal structure is built up of a succession of close-packed layers of identical structure, but stacked on top of each other in alternative ways (Figure 3.24). The simplest kind of SiC simply repeats steps ABCABC, etc., and the step height corresponds to three layers only. Many other stacking sequences



Figure 3.23. A growth spiral on a silicon carbide crystal, originating from the point of emergence of a screw dislocation (courtesy Prof. S. Amelinckx).

are found, for instance, ABCACBCABACBCB; for this “15R” structure, the repeat height must be five times larger than for an ABC sequence. Such polytypes can have 33 or even more single layers before the sequence repeats. Verma was eventually able to show that in all polytypes, spiral step height matched the height of the expanded unit cell, and later he did the same for other polytypic crystals such as CdI_2 and PbI_2 . The details can be found in an early book (Verma 1953) and in the aforementioned autobiographical memoir. Like all the innovations outlined here, polytypism has been the subject of burgeoning research once growth spirals had been detected; one recent study related to polytypic phase transformations: dislocation mechanisms have been detected that can transform one polytype into another (Pirouz and Yang 1992).

The varying stacking sequences, when they are found irregularly rather than reproducibly, are called *stacking faults*; these are one of several forms of two-dimensional crystal defects, and are commonly found in metals such as cobalt where there are two structures, cubic and hexagonal close-packed, which differ very little in free energy. Such stacking faults are also found as part of the configuration of edge dislocations in such metals; single dislocations can split up into partial dislocations,

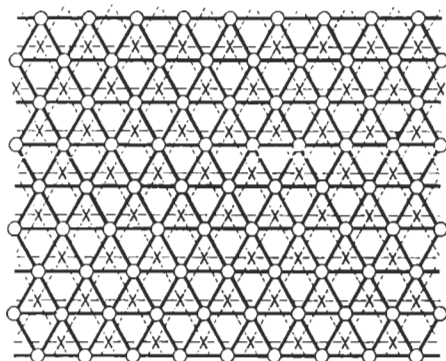


Figure 3.24. Projection of silicon carbide on the (0 0 0 1) plane (after Verma 1953).

separated by stacking faults, and this splitting has substantial effects on mechanical behaviour. William Shockley with his collaborator R.D. Heidenreich was responsible for this discovery, in 1948 just after he had helped to create the first transistor.

Stacking faults and sometimes proper polytypism are found in many inorganic compounds – to pick out just a few, zinc sulphide, zinc oxide, beryllium oxide. Interest in these faults arises from the present-day focus on electron theory of phase stability, and on computer simulation of lattice faults of all kinds; investigators are attempting to relate stacking-fault concentration on various measurable characteristics of the compounds in question, such as “ionicity”, and thereby to cast light on the electronic structure and phase stability of the two rival structures that give rise to the faults.

3.2.3.5 Crystal structure, crystal defects and chemical reactions. Most chemical reactions of interest to materials scientists involve at least one reactant in the solid state: examples include surface oxidation, internal oxidation, the photographic process, electrochemical reactions in the solid state. All of these are critically dependent on crystal defects, point defects in particular, and the thermodynamics of these point defects, especially in ionic compounds, are far more complex than they are in single-component metals. I have space only for a superficial overview.

Two German physical chemists, W. Schottky and C. Wagner, founded this branch of materials science. The story is very clearly set out in a biographical memoir of Carl Wagner (1901–1977) by another pioneer solid-state chemist, Hermann Schmalzried (1991), and also in Wagner’s own survey of “point defects and their interaction” (Wagner 1977) – his last publication. Schottky we have already briefly met in connection with the Pohl school’s study of colour centres

(Section 3.2.3.1). Wagner built his early ideas on the back of a paper by a Russian, J. Frenkel, who first recognised that in a compound like AgBr some Ag ions might move in equilibrium into interstitial sites, balancing a reduction in internal energy because of favourable electrostatic interactions against entropy increase. Wagner and Schottky (Wagner and Schottky 1930, Wagner 1931) treated point defects in metallic solid solutions and then also ionic crystals in terms of temperature, pressure and chemical potential as independent variables; these were definitive papers. Schmalzried asserts firmly that “since the thirties, it has remained an undiminished challenge to establish the defect types in equilibrated crystals. Predictions about defect-conditioned crystal properties (and that includes inter alia all reaction properties) are possible only if types and concentrations of defects are known as a function of the chemical potentials of the components.” Wagner, in a productive life, went on to study chemical reactions in solids, especially those involving electrical currents, diffusion processes (inseparable from reactions in solids). For instance, he did some of the first studies on stabilised zirconia, a crucial component of a number of chemical sensors: he was the first to recognise (Wagner 1943) that in this compound, it is the ions and not the electrons which carry the current, and thus prepared the way for the study of superionic conductors which now play a crucial role in advanced batteries and fuel cells. Wagner pioneered the use of intentionally non-stoichiometric compounds as a way of controlling point-defect concentrations, with all that this implies for the control of compound (oxide) semiconductors. He also performed renowned research on the kinetics and mechanism of surface oxidation and, late in his life, of ‘Ostwald ripening’ (the preferential growth of large precipitates at the cost of small ones). There was a scattering of other investigations on defects in inorganic crystals; one of the best known is the study of defects in ferrous oxide, FeO, by Foote and Jette, in the first issue of *Journal of Chemical Physics* in 1933, already mentioned in Section 2.1.1. The systematic description of such defects, in ionic crystals mostly, and their interactions formed the subject-matter of a remarkable, massive book (Kröger 1964); much of it is devoted to what the author calls “imperfection chemistry”.

The subject-matter outlined in the last paragraph also forms the subject-matter of a recent, outstanding monograph by Schmalzried (1995) under the title *Chemical Kinetics of Solids*. While the role of point defects in governing chemical kinetics received pride of place, the role of dislocations in the heterogeneous nucleation of product phases, a neglected topic, also receives attention; the matter was analysed by Xiao and Haasen (1989). Among many other topics, Wagner’s theory of oxidation receives a thorough presentation. It is rare to find different kinds of solid-state scientists brought together to examine such issues jointly; one rare example was yet another Faraday Discussion (1959b) on *Crystal Imperfections and the Chemical Reactivity of Solids*. Another key overview is a book by Rao and Gopalakrishnan

(1986, 1997) which introduces defects and in a systematic way relates them to non-stoichiometry, including the 'shear planes' which are two-dimensional defects in off-stoichiometric compounds such as the niobium oxides. This book also includes a number of case-histories of specific compounds and also has a chapter on the *design* of a great variety of chemicals to fulfil specified functional purposes. Yet another excellent book which covers a great variety of defects, going far beyond simple point defects, is a text entitled *Disorder in Crystals* (Parsonage and Staveley 1978). It touches on such recondite and apparently paradoxical states as 'glassy crystals' (also reviewed by Cahn 1975): these are crystals, often organic, in which one structural component rotates freely while another remains locked immobile in the lattice, and in which the former are then 'frozen' in position by quenching. These in turn are closely related to so-called 'plastic crystals', in which organic constituents are freely rotating: such crystals are so weak that they will usually deform plastically merely under their own weight.

A word is appropriate here about the most remarkable defect-mediated reaction of all – the photographic process in silver bromide. The understanding of this in terms of point defects was pioneered in Bristol by Mott and Gurney (1940, 1948).⁴ The essential stages are shown in Figure 3.25: the important thing is that a captured photon indirectly causes a neutral silver atom to sit on the surface of a crystallite. It was subsequently established that a nucleus of only 4 atoms suffices; this is large enough to be developable by subsequent chemical treatment which then turns the whole crystallite into silver, and contributes locally to the darkening of the photographic emulsion. AgBr has an extraordinary range of physical properties, which permit light of long wavelengths to be absorbed and generate electron/hole pairs at very high efficiencies (more than 10% of all photons are thus absorbed). The photoelectrons have an unusually long lifetime, several microseconds. Also, only a few surface sites on crystallites manage to attract all the silver ions so that the 4-atom nuclei form very efficiently. The American physicist Lawrence Slifkin (1972, 1975) has analysed this series of beneficial properties, and others not mentioned here, and estimates the probability of the various separate physical properties that must come together to make high-sensitivity photography possible. The product of all these independent probabilities $\approx 10^{-8}$ and it is thus not surprising that all attempts to find a cheaper, efficient substitute for AgBr have uniformly failed (unless one regards the recently introduced digital (filmless) camera as a substitute). Slifkin asserts baldly: "The photographic process is a miracle – well, perhaps not quite a miracle, but certainly an extraordinary phenomenon".

⁴ Frederick Seitz has recently remarked (Seitz 1998) that he has long thought that Nevill Mott deserved the Nobel Prize for this work alone, and much earlier in his career than the Prize he eventually received.

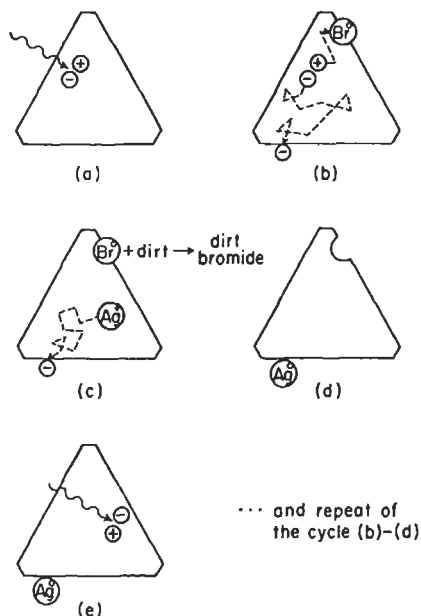


Figure 3.25. The Gurney-Mott model for the formation of a latent image (after Slifkin 1972).

Yet another category of chemical behaviour which is linked to defects, including under that term ultrasmall crystal size and the presence of uniformly sized microchannels which act as filters for molecules of different sizes, is *catalysis*. It is open to discussion whether heterogeneous catalysis, a field of very great current activity, belongs to the domain of materials science, so nothing more will be said here than to point the reader to an outstanding historical overview by one of the main protagonists, Thomas (1994). He starts his account with Humphry Davy's discovery at the Royal Institution in London that a fine platinum wire will glow when in contact with an inflammable mixture (e.g., coal gas and air) and will remain so until the mixture is entirely consumed. This then led a German, Döbereiner, to produce a gas-lighter based upon this observation. It was some considerable time before advances in surface science allowed this observation to be interpreted; today, catalysis is a vast, commercially indispensable and very sophisticated branch of materials design.

3.2.4 Crystal chemistry and physics

The structure of sodium chloride determined by the Braggs in 1913 was deeply disturbing to many chemists. In a letter to *Nature* in 1927, Lawrence Bragg made

(not for the first time) the elementary point that “In sodium chloride there appear to be no molecules represented by NaCl. The equality in number of sodium and chlorine atoms is arrived at by a chessboard pattern of these atoms; it is a result of geometry and not of a pairing-off of the atoms.” The irrepressible chemist Henry Armstrong, whom we have already met in Chapter 2 pouring ridicule on the pretensions of the ‘ionists’ (who believed that many compounds on dissolving in water were freely dissociated into ions), again burst into print in the columns of *Nature* (Armstrong 1927) to attack Bragg’s statement as “more than repugnant to common sense, as absurd to the *n*th degree, not chemical cricket. Chemistry is neither chess nor geometry, whatever X-ray physics may be. Such unjustified aspersion of the molecular character of our most necessary condiment must not be allowed any longer to pass unchallenged”. He went on to urge that “it were time that chemists took charge of chemistry once more and protected neophytes against the worship of false gods...” One is left with the distinct impression that Armstrong did not like ions! Two years earlier, also in *Nature*, he had urged that “dogmatism in science is the negation of science”. He never said a truer word.

This little tale reveals the difficulties that the new science of crystal structure analysis posed for the chemists of the day. Lawrence Bragg’s own researches in the late 1920s, with W.H. Taylor and others, on the structures of a great variety of silicates and their crucial dependence on the Si/O ratio required completely new principles of what came to be called *crystal chemistry*, as is described in a masterly retrospective overview by Laves (1962). The crucial intellectual contribution came from a Norwegian geochemist of genius, Viktor Moritz Goldschmidt (1888–1947) (Figure 3.26); his greatest work in crystal chemistry, a science which he created, was done between 1923 and 1929, even while Bragg was beginning to elucidate the crystal structures of the silicates.

Goldschmidt was born in Switzerland of Jewish parents, his father a brilliant physical chemist; he was initially schooled in Amsterdam and Heidelberg but moved to Norway at the age of 13 when his father became professor in Oslo. Young Goldschmidt himself joined the university in Christiania (=Oslo) to study chemistry (with his own father), mineralogy and geology, three disciplines which he later married to astonishing effect. He graduated young and at the age of 23 obtained his doctorate, a degree usually obtained in Norway between the ages of 30 and 40. He spent some time roaming Europe and learning from masters of their subjects such as the mineralogist Groth, and his initial researches were in petrography – that is, mainline geology. In 1914, at the age of 26, he applied for a chair in Stockholm, but the usually ultra-sluggish Norwegian academic authorities moved with lightning speed to preempt this application, and before the Swedish king had time to approve the appointment (this kind of formality was and is common in Continental universities), Oslo University got in first and made him an unprecedentedly young



Figure 3.26. Viktor Goldschmidt (courtesy Royal Society).

professor of mineralogy. 15 years later, he moved to Göttingen, but Nazi persecution forced him to flee back to Norway in 1935, abandoning extensive research equipment that he had bought with his own family fortune. Then, during the War, he again had a very difficult time, especially since he used his geological expertise to mislead the Nazi occupiers about the location of Norwegian mineral deposits and eventually the Gestapo caught up with him. Again, all his property was confiscated; he just avoided being sent to a concentration camp in Poland and escaped via Sweden to Britain. After the War he returned once more to Norway, but his health was broken and he died in 1947, in a sad state of paranoia towards his greatest admirers. He is generally regarded as Norway's finest scientist.

There are a number of grim anecdotes about him in wartime; thus, at that time he always carried a cyanide capsule for the eventuality of his capture, and when a fellow professor asked him to find him one too, he responded: "This poison is for professors of chemistry only. You, as a professor of mechanics, will have to use the rope".

For our purposes, the best of the various memoirs of Goldschmidt are a lecture by the British crystallographer and polymath John Desmond Bernal (Bernal 1949),

delivered in the presence of Linus Pauling who was carrying Goldschmidt's work farther still, and the Royal Society obituary by an eminent petrologist (Tilley 1948–1949). For geologists, Goldschmidt's main claim to fame is his systematisation of the distribution of the elements geochemically, using his exceptional skills as an analytical inorganic chemist. His lifetime's geochemical and mineralogical researches appeared in a long series of papers under the title "Geochemical distribution laws of the elements". For materials scientists, however, as Bernal makes very clear, Goldschmidt's claim to immortality rests upon his systematisation of crystal chemistry, which in fact had quite a close linkage with his theories concerning the factors that govern the distribution of elements in different parts of the earth.

In the course of his work, he trained a number of eminent researchers who inhabited the borderlands between mineralogy and materials science, many of them from outside Norway – e.g., Fritz Laves, a German mineralogist and crystal chemist, and William Zachariasen, a Norwegian who married the daughter of one of Goldschmidt's Norwegian teachers and became a professor in Chicago for 44 years; he first, in the 1930s, made fundamental contributions to crystal structure analysis and to the understanding of glass structure (Section 7.5), then (at Los Alamos during the War) made extensive additions to the crystallography of transuranium elements (Penneman 1982). Incidentally, Zachariasen obtained his Oslo doctorate at 22, even younger than his remarkable teacher had done. Goldschmidt's own involvement with many lands perhaps led his pupils to become internationalists themselves, to a greater degree than was normal at the time.

During 1923–1925 Goldschmidt and his collaborators examined (and often synthesized) more than 200 compounds incorporating 75 different elements, analysed the natural minerals among them by X-ray fluorescence (a new technique based on Manne Siegbahn's discoveries in Sweden) and examined them all by X-ray diffraction. His emphasis was on oxides, halides and sulphides. A particularly notable study was of the rare-earth sesquioxides (A_2X_3 compounds), which revealed three crystal structures as he went through the lanthanide series of rare-earth elements, and from the lattice dimensions he discovered the renowned 'lanthanide contraction'. He was able to determine the standard sizes of both cations and anions, which differed according to the charge on the ion. He found that the ratio of ionic radii was the most important single factor governing the crystal structure because the *coordination number* of the ions was governed by this ratio. For Goldschmidt, coordination became *the* governing factor in crystal chemistry. Thus simple binary AX compounds had 3:3 coordination if the radius ratio < 0.22 , 4:4 if it was in the range 0.22–0.41, 6:6 up to 0.73 and 8:8 beyond this. This, however, was only the starting-point, and general rules involving (a) numerical proportions of the constituent ions, (b) radius ratios, (partly governed by the charge on each kind of ion) and (c) polarisability of large anions and polarising power of small cations

which together determined the shape distortion of ions, governed crystal structures of ionic compounds and also their geochemical distributions. All this early work was published in two classical (German-language) papers in Norway in 1926.

Later in the 1920s he got to work on covalently bonded crystals and on intermetallic compounds and found that they followed different rules. He confirmed that normal valency concepts were inapplicable to intermetallic compounds. He established the 'Goldschmidt radii' of metal atoms, which are a function of the coordination number of the atoms in their crystal structures; for many years, all undergraduate students of metallurgy learnt about these radii at an early stage in their education. Before Goldschmidt, ionic and atomic radii were vague and handwaving concepts; since his work, they have been precise and useful quantities. It is now recognised that such radii are not strictly constant for a particular coordination number but vary somewhat with bond length and counter-ion to which a central ion is bonded (e.g., Gibbs *et al.* 1997), but this does not detract from the great practical utility of the concepts introduced by Goldschmidt.

Together with the structural principles established by the Bragg school concerning the many types of silicates, Goldschmidt's ideas were taken further by Linus Pauling in California to establish the modern science of crystal chemistry. A good early overview of the whole field can be found in a book by Evans (1939, 1964).

In his heyday, Goldschmidt "was a man of amazing energy and fertility of ideas. Not even periods of illness could diminish the ardour of his mind, incessantly directed to the solution of problems he set himself" (Tilley). His knowledge and memory were stupendous; Max Born often asked him for help in Göttingen and more often than not Goldschmidt was able to dictate long (and accurate) tables of figures from memory. This ability went with unconventional habits of organisation. According to Tilley, "he remembered at once where he had buried a paper he wanted, and this was all the more astonishing as he had a system not to tidy up a writing-desk but to start a new one when the old one was piled high with papers. So gradually nearly every room in his house came to have a writing-desk until there was only a kitchen sink in an unused kitchen left and even this was covered with a board and turned to the prescribed use."

Perhaps the most influential of Goldschmidt's collaborators, together with W.H. Zachariasen, was the German Fritz Laves (1906–1978), who (after becoming devoted to mineralogy as a 12-year-old when the famous Prof. Mügge gave him the run of his mineralogical museum) joined Goldschmidt in Göttingen in 1930, having taken his doctorate with Paul Niggli (a noted crystallographer/mineralogist) in Zürich. He divided his most active years between several German universities and Chicago (where Zachariasen also did all his best work). Laves made his name with the study of feldspars, one of the silicate families which W.L. Bragg was studying so successfully at the same time as Laves's move to Göttingen. He continued

Goldschmidt's emphasis on the central role of geometry (radius ratios of ions or atoms) in determining crystal structure. The additional role of electronic factors was identified in England a few years later (see Section 3.3.1, below). A good example of Laves's insights can be found in a concise overview of the crystal structures of intermetallics (Laves 1967). A lengthy obituary notice in English of Laves, which also gives an informative portrait of the development of mineralogical crystallography in the 20th century and provides a complete list of his publications, is by Hellner (1980).

3.2.5 Physical mineralogy and geophysics

As we have seen, mineralogy with its inseparable twin sister, crystallography, played a crucial role in the establishment of the atomic hypothesis. For centuries, however, mineralogy was a systematiser's paradise (what Rutherford called 'stamp-collecting') and modern science really only touched it in earnest in the 1920s and 1930s, when Goldschmidt and Laves created crystal chemistry. In a survey article, Laves (1959) explained why X-ray diffraction was so late in being applied to minerals in Germany particularly: traditionally, crystallography belonged to the great domain of the mineralogists, and so the physicists, who were the guardians of X-ray diffraction, preferred to keep clear, and the mineralogists were slow to pick up the necessary skills.

While a few mineralogists, such as Groth himself, did apply physical and mathematical methods to the study of minerals, tensor descriptions of anisotropy in particular – an approach which culminated in a key text by Nye (1957) – 'mineral physics' in the modern sense did not get under way until the 1970s (Poirier 1998), and then it merged with parts of modern geophysics. A geophysicist, typically, is concerned with physical and mechanical properties of rocks and metals under extremely high pressure, to enable him to interpret heat flow, material transport and phase transformations of material deep in the earth (including the partially liquid iron core). The facts that need to be interpreted are mostly derived from sophisticated seismometry. Partly, the needed information has come from experiments, physical or mechanical, in small high-pressure cells, including diamond cells which allow X-ray diffraction under hydrostatic pressure, but lately, first-principles calculations of material behaviour under extreme pressure and, particularly, computer simulation of such behaviour, have joined the geophysicist's/mineralogist's armoury, and many of the scientists who have introduced these methods were trained either as solid-state physicists or as materials scientists. They also brought with them basic materials scientist's skills such as transmission electron microscopy (D. McConnell, formerly in Cambridge and now in Oxford, was probably the first to apply this technique to minerals), and crystal mechanics. M.S. Paterson in Canberra,

Australia, is the doyen of materials scientists who study the elastic and plastic properties of minerals under hydrostatic pressure and also phase stability under large shear stresses (Paterson 1973). J.-P. Poirier, in Paris, a professor of geophysics, was trained as a metallurgist; one of his special skills is the use of analogue materials to help understand the behaviour of inaccessible high-pressure polymorphs, e.g., CaTiO_3 perovskite to stand in for $(\text{Mg}, \text{Fe})\text{SiO}_3$ in the earth's mantle (Poirier 1988, Besson *et al.* 1996).

A group of physicists and chemists at the atomic laboratory at Harwell, led by A.M. Stoneham, were among the first to apply computer simulation techniques (see Chapter 12) to minerals; this approach is being energetically pursued by G.D. Price at University College, London: an example is the computer-calculation of ionic diffusion in MgO at high temperatures and pressures (Vocadlo *et al.* 1995); another impressive advance is a study of the melting behaviour of iron at pressures found at the earth's core, from *ab initio* calculations (Alfè *et al.* 1999). This was essential for getting a good understanding of the behaviour of iron in the core; its melting temperature at the relevant pressure was computed to be 6670 K. In a commentary on this research, in the same issue of *Nature*, Bukowinski remarks that "the earth can be thought of as a high-pressure experiment, a vast arena for the interplay of geophysical observation with experimental and computational materials science. For research, it is a clear win-win situation".

'Computational mineralogy' has now appeared on the scene. First-principles calculations have been used, inter alia, to estimate the transport properties of both solid and molten iron under the extreme pressures characteristic of the earth's core (Vocadlo *et al.* 1997). The current professor of mineralogy, Ekhard Salje, in Cambridge's Department of Earth's Sciences is by origin a mathematical physicist, and he uses statistical mechanics and critical theory to interpret phenomena such as ferroelasticity in minerals; he also applies lessons garnered from the study of minerals to the understanding of high-temperature superconductors. Generally, modern mineralogists and geophysicists interact much more freely with various kinds of materials scientists, physicists, solid-state chemists and engineers than did their predecessors in the previous generation, and new journals such as *Physics and Chemistry of Minerals* have been created.

3.3. EARLY ROLE OF SOLID-STATE PHYSICS

To recapitulate, the legs of the imaginary tripod on which the structure of materials science is assembled are: atoms and crystals; phase equilibria; microstructure. Of course, these are not wholly independent fields of study. Microstructure consists of phases geometrically disposed, phases are controlled by Gibbsian thermodynamics,

crystal structures identify phases. Phases and their interrelation can be understood in physical terms; in fact, Gibbsian thermodynamics are a major branch of physics, and one expert in statistical physics has characterised Gibbs as “a great pioneer of modern physics”. To round out this long chapter, it is time now to outline the physical underpinning of modern materials science.

3.3.1 *Quantum theory and electronic theory of solids*

When Max Planck wrote his remarkable paper of 1901, and introduced what Stehle (1994) calls his “time bomb of an equation, $\epsilon = h\nu$ ”, it took a number of years before anyone seriously paid attention to the revolutionary concept of the quantisation of energy; the response was as sluggish as that, a few years later, which greeted X-ray diffraction from crystals. It was not until Einstein, in 1905, used Planck’s concepts to interpret the photoelectric effect (the work for which Einstein was actually awarded his Nobel Prize) that physicists began to sit up and take notice. Niels Bohr’s thesis of 1911 which introduced the concept of the quantisation of electronic energy levels in the free atom, though in a purely empirical manner, did not consider the behaviour of atoms assembled in solids.

It took longer for quantum ideas to infect solid-state physics; indeed, at the beginning of the century, the physics of the solid state had not seriously acquired an identity. A symposium organised in 1980 for the Royal Society by Nevill Mott under the title of *The Beginnings of Solid State Physics* (Mott 1980) makes it clear that there was little going on that deserved the title until the 1920s. My special concern here is the impact that quantum theory had on the theory of the behaviour of electrons in solids. In the first quarter of the century, attention was focused on the Drude–Lorentz theory of free electrons in metals; anomalies concerning the specific heat of solids proved obstinately resistant to interpretation, as did the understanding of why some solids conducted electricity badly or not at all. Such issues were destined to continue to act as irritants until quantum theory was at last applied to the theory of solids, which only happened seriously after the creation of wave mechanics by Erwin Schrödinger and Werner Heisenberg in 1926, the introduction of Pauli’s exclusion principle and the related conception of Fermi–Dirac statistics in the same year. This familiar story is beyond my remit here, and the reader must turn to a specialist overview such as that by Rechenberg (1995).

In the above-mentioned 1980 symposium (p. 8), the historians Hoddeson and Baym outline the development of the quantum-mechanical electron theory of metals from 1900 to 1928, most of it in the last two years of that period. The topic took off when Pauli, in 1926, examined the theory of paramagnetism in metals and proved, in a famous paper (Pauli 1926) that the observations of weak paramagnetism in various metals implied that metals obeyed Fermi–Dirac statistics – i.e., that the electrons in

metals obeyed his exclusion principle. Soon afterwards, Arnold Sommerfeld applied these statistics to generate a hybrid classical-quantum theory of metals (the story is outlined by Hoddeson and Baym), but real progress was not made until the band theory of solids was created. The two key early players were Felix Bloch, who in 1928 applied wave mechanics to solids, treating ‘free’ electrons as waves propagating through the lattice, *unscattered by the individual stationary metal ions constituting the lattice*, and Léon Brillouin (1930) who showed that some of these same electron waves must be diffracted by planes of ions when the Bragg Law was satisfied – and this, in turn, limited the velocities at which the electrons can migrate through the lattice. Bloch (in Mott 1980, p. 24) offers his personal *memories of electrons in crystals*, starting with his thesis work under Heisenberg’s direction which began in 1927. The best place to read the history of these developments in clear, intelligible terms is in Pippard’s treatment of “electrons in solids” (Pippard 1995) – which here largely means electrons in metals; this excellent account starts with Drude–Lorentz and the complexities of the early work on the Hall Effect and thermoelectricity, and goes on to modern concerns such as magnetoresistance... but the heroic era was concentrated in the years 1926–1930.

The other place to read an authoritative history of the development of the quantum-mechanical theory of metals and the associated evolution of the band theory of solids is in Chapters 2 and 3 of the book, *Out of the Crystal Maze*, which is a kind of official history of solid-state physics (Hoddeson *et al.* 1992).

The recognition of the existence of semiconductors and their interpretation in terms of band theory will be treated in Chapter 7, Section 7.2.1. Pippard, in his chapter, includes an outline account of the early researches on semiconductors.

Pippard, in his historical chapter, also deals with some of his own work which proved to have a notable effect on theoretical metallurgy in the 1950s. The “anomalous skin effect”, discovered in 1940, is an enhanced electrical resistivity in the surface layers of a (non-superconductive) metal when tested with a high-frequency field; at high frequencies, most of the current is restricted to a surface “skin”. Sondheimer (1954) developed the theory of this effect and showed its relation to the form of the Fermi surface, the locus of the maximum possible electron kinetic energies in a solid ion in different crystal directions. This was initially taken to be always spherical, but Pippard himself was stimulated by Sondheimer’s work to make experiments on the anomalous skin effect in copper crystals and succeeded, in a virtuoso piece of research, in making the first determination (Pippard 1957) of the true shape of a Fermi surface (Figure 3.27). The figure is drawn in k -space... i.e., each vector from the origin represents an electron moving with a momentum (k) defined by the vector.

One other classical pair of papers should be mentioned here. Eugene Wigner, an immigrant physicist of Hungarian birth, and his student Frederick Seitz whom we

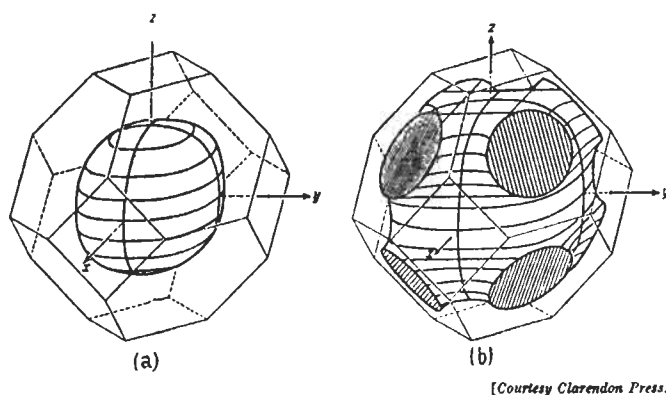


Figure 3.27. The first Brillouin zone of the face-centred cubic structure, after Pippard.

have already met (Figure 3.19) wrote theoretical papers (Wigner and Seitz 1933, 1934) about the origin of the cohesion of solid sodium – i.e., what holds the metal together. They chose this esoteric metal because it was easier to handle with acceptable accuracy than the more familiar metals. The task was to calculate the wave-function of the free (valence) electrons in the neighbourhood of a sodium ion: in very simplified terms, the valence electrons have greater freedom in the metal than in the isolated atom, and the potential energy of an electron in the regions between ions is less than at the same distance from an isolated atom. This circumstance in effect holds the ions together in the lattice. The methods used by Wigner and Seitz to make these calculations are still frequently cited, and in fact these two papers are regarded by many as marking the effective birth of modern solid-state physics. The success of his collaboration with Wigner encouraged Seitz to write the first comprehensive book on solid-state physics, *The Modern Theory of Solids* (Seitz 1940), which must have alerted thousands of students of the solid state to the central importance of quantum theory. About this extremely influential book, Seitz, in a recent autobiography, has remarked with undue modesty: “It has since been reissued by Dover Press and presumably possesses at least archaeological value” (Seitz 1994, p. 83).

24 years later, another standard text, *Physics of Solids*, was brought out by Wert and Thomson (1964). In his foreword to this book, Seitz has this to say: “This fine book, which was inspired by my old book but has outgrown it in almost all respects, is a preparatory text for the young engineer of today. A generation ago *it would have provided sound material for a graduate student of physics with an interest in solid-state science* (my emphasis). The fact that it is written by two members of a modern active metallurgy department (at the University of Illinois) demonstrates that a field of engineering has now reached out to absorb another newly developed field of science

which has a significant bearing on the areas of technology which this field of engineering serves.”

The critical attitude towards the physical study of solids which some eminent physicists in the 1930s evinced was based on their view that solids were irremediably dirty, messy entities, semiconductors especially. On a famous occasion in 1933 (recorded in Chapter 2 of the Hoddeson book) when the youthful Peierls showed his adviser, Pauli, some calculations relating to the residual electrical resistivity in (impure) solids, Pauli burst out: “I consider it harmful when younger physicists become accustomed to order-of-magnitude physics. The residual resistivity is a dirt effect, and one shouldn’t wallow in dirt”. The fierceness of the attack emerges better from the original German: “...im Dreck soll man nicht wühlen”. In part this attitude was also a reaction against the experimental work in Pohl’s institute at Göttingen where colour centres in intentionally doped ionic crystals were systematically studied. One of those who was infected by this critical attitude was the eminent American physicist Isidore Rabi (1898–1988), who spent some years in Germany in the 1920s. To one of his graduate students at Columbia University, towards the end of the 1940s, he declared: “The physics department at Columbia will never occupy itself with the physics of dirt”. Ironically, he said this just as the transistor, which depends on controlled impurities, was being developed at the Bell Laboratories.

3.3.1.1 Understanding alloys in terms of electron theory. The band theory of solids had no impact on the thinking of metallurgists until the early 1930s, and the link which was eventually made was entirely due to two remarkable men – William Hume-Rothery in Oxford and Harry Jones in Bristol, the first a chemist by education and the second a mathematical physicist.

Hume-Rothery (1899–1968; Figure 3.28; for biographical memoirs, see Raynor 1969 and Pettifor 2000) was educated as a chemist in Oxford, where he spent all of his later scientific career, but took his Ph.D. at Imperial College, London, with Harold Carpenter, the professor of metallurgy there (we shall meet him again in Section 4.2.1), on the structure and properties of intermetallic compounds. Such compounds were sure to interest a bright chemist at a time when the nature of valence was a leading concern in chemistry, since they do not follow normal valence rules: the experience converted Hume-Rothery into a dedicated metallurgist who eventually, after sustained struggles, succeeded in introducing metallurgy as a fully fledged undergraduate subject at Oxford University from 1949 – rather later than in Cambridge. For 23 years he performed his notable researches, initially at a single bench in a small room, without longterm security as a Warren Research Fellow of the Royal Society, before eventually his admirers provided the means for creating first a Readership (associate professorship) and soon after, an endowed chair of

metallurgy. He was in frequent communication with, and had the support of, many of the notable chemists and physicists of his time, notably the physical chemist Cyril Hinshelwood in Oxford and the theoretical physicist Nevill Mott (1905–1996, Figure 3.18) in Bristol. Mott has already appeared many times in this chapter, especially in connection with dislocation theory, and his role in the evolution of modern materials science was massive.

In a brief note in Mott's historical symposium (Mott 1980, p. 54), written after Hume-Rothery's death, B.R. Coles (a metallurgist turned experimental physicist... it does sometimes happen) remarked that "Hume-Rothery was the first to recognise explicitly that one should regard a random substitutional alloy of two metals as a giant molecule possessing an electron gas to which both components contributed. The essential quantity of interest was therefore the average number of outer electrons per atom...". He and his students determined a number of phase diagrams, especially of alloys based on copper, silver and gold, with great precision and then worked out regularities governing the appearance of successive intermetallic phases in these systems. Starting with a precocious key paper (Hume-Rothery 1926) and culminating in a classic paper on silver- and copper-based phases (Hume-Rothery *et al.* 1934), Hume-Rothery established empirically that the successive phases turned up at specific values (such as $3/2$ or $21/13$) of the ratio of free (valence) electrons to metallic atoms. Since solvent and solute in general bring different numbers of valence electrons into the alloys, this ratio is bound to change as the solute concentration increases. The phases thus examined by Hume-Rothery became known as *electron phases*. The precision study of phase diagrams and conclusions drawn from them continued for many years thereafter, and he also followed in the footsteps of Moritz Goldschmidt (a near-contemporary) by focusing on the role of atomic size in governing solubilities. This in turn led to a sustained programme of analysing the stability of alloy phases in the light of their lattice parameters.

Harry Jones, as a young researcher in Mott's physics department in Bristol heard about Hume-Rothery's empirical regularities in a lecture by W.L. Bragg in 1932 or 1933 (see Jones 1980), and at once began trying to understand the reasons for the formation of γ -brass, Cu_5Zn_8 , the crystal structure of which had been determined by one of Bragg's students, Albert Bradley. The Jones theory, to simplify drastically, was based on the notion that as polyvalent solute (Zn) is added to monovalent face-centred cubic solvent (Cu), the (supposedly) spherical Fermi surface expands and eventually touches the first Brillouin zone (Figure 3.27). When that happens, the density of electronic energy states changes drastically, and that in turn, by simple arguments, can be shown to raise the Gibbsian free energy of the initial phase sufficiently for an alternative crystal structure to become stabilised instead. In that way, first the β -brass and subsequently the γ -brass structure become stabilised. A theory based purely on the quantum theory of electrons in solids had thereby been

shown to interpret a set of metallurgical observations on phase stability (Jones 1934). This work became much more widely known after the publication of a key theoretical book by Mott and Jones (1936), still frequently cited today.

Hume-Rothery popularised his findings, and also the theoretical superstructure initiated by Jones, in a series of influential books, beginning with a 1931 volume (*The Metallic State*) and peaking with *The Structure of Metals and Alloys*, first published in 1936 by the Institute of Metals in London and updated through many editions over the years with a number of distinguished coauthors. Another, more elementary book, republished from short articles in an industrial metallurgy journal, consisted of conversations between an older and a younger metallurgist. He encountered much opposition from those older metallurgists (like the steelmaker, Harry Brearley, whom we have already met) who even thought that their professional body, the Institute of Metals, had no business publishing such a cloudy volume as *The Structure of Metals and Alloys*, but Hume-Rothery persisted and succeeded in transforming metallurgical education, starting with the Department of Physical Metallurgy at Birmingham University where Geoffrey Raynor, Hume-Rothery's most distinguished student, from 1948 spread the 'gospel' of the new metallurgy. The



Figure 3.28. William Hume-Rothery as a young man (courtesy Mrs. Jennifer Moss).

reader will recall that in 1917, Rosenhain was proselytising for his own 'new metallurgy'; 20 years later, Hume-Rothery was rewriting the meaning of 'new' in that pregnant phrase. Many books followed Hume-Rothery's in successive attempts to interpret modern electron theory of metals to scientists trained as metallurgists or materials scientists; notable examples are books by Cottrell (1988) and by Pettifor and Cottrell (1992), in addition to Cottrell's classic textbook of 1948 which we have already met.

At one point it seemed that the entire theoretical superstructure advanced to explain Hume-Rothery's electron phases had collapsed, because of Pippard's (1957) discovery that the Fermi surface of pure copper was not after all spherical and already touched the first Brillouin zone *even before any polyvalent solute was added* (Figure 3.27, right). This seemed to remove the essential concept from Jones's theory, and thus the agreement between Hume-Rothery's experimental findings and Jones's theory appeared to be merely fortuitous. But, as the science-historian Gerald Holton once remarked, "The graveyard of failed scientists is littered with those who did not suspend disbelief when their ideas were first shown to be wrong". In due course, the apparent disaster was seen not to be one after all. Cottrell, in a little textbook on electron theory published just half a century after his first book (Cottrell 1998) explains what happened: Because of the absence of computers in the 1930s, Jones had to make a number of simplifying approximations in developing his theory, one being the so-called "rigid-band approximation" – that the form of the density-of-states distribution remains fixed as the electron-to-atom ratio increases, another being that the Fermi surface remains spherical even when it touches a Brillouin zone boundary. Even though Jones modified some of his approximations in 1937, Pippard's study still seemed to undermine the theory, but in fact it became clear later that some of the theoretical errors revealed by this study cancelled each other. (This is a not uncommon experience in the history of theoretical science.) The new theory (Paxton *et al.* 1997) avoids Jones's approximations, takes proper account of the influence of *d* electrons (which Jones could not do), and, in Cottrell's words: "The modern theory, by taking full advantage of present-day computer power, has been able to avoid both approximations and so, because of their mutual cancellation, has achieved the same success – or even better – but on an intrinsically more sound basis".

Hume-Rothery's position as one of the key creators of modern physical metallurgy remains unchallenged.

Hume-Rothery's ideas and their theoretical development by Mott and Jones stimulated much consequential research around the world. The most impressive early 'convert' was a French physicist, Jacques Friedel, who should have been mentioned in connection with dislocations, in the theory of which he played an early part (see the Corrigenda). After a very disturbed war, which ranged from study at the

Ecole Polytechnique to work down a coalmine, he resolved to make himself an expert in quantum mechanics, a theme until then gravely neglected in France, and decided that the place to learn it was as a doctoral student with Nevill Mott in Bristol. The idea of going abroad to study a branch of physics in depth was at that time novel among the French. In his autobiography (Friedel 1994), he describes “le choc de Bristol (1949–1952)” and the difficulties he had in being assigned a research topic that fitted his objective. He finally wrote his thesis on the electron theory of metallic solid solutions, in which he became a renowned innovator. A first account was published soon after (Friedel 1952) and some more sophisticated developments followed later, notably his treatment of the distribution of conduction electrons round an alloy atom of valency different from that of the host. The screening charge was shown (Friedel 1958) to exist as a series of concentric haloes, of higher and lower electron density, around a dissolved solute atom...the ‘Friedel oscillations’. A number of other developments followed later, and Friedel created a distinguished school in Paris with offshoots elsewhere in France. An account of his role, from a French perspective, is given in a book chapter devoted to the history of solid-state physics in France (Guinier 1988).

Meanwhile, electron theory was revived effectively in Hume-Rothery’s own base of Oxford, and is now led by a distinguished mathematical physicist, David Pettifor.

Nevill Mott, first in Bristol and then in Cambridge, has repeatedly surfaced in this chapter; a few more words about his remarkable personality are in order here. He was a superb theorist who interacted effortlessly with experimentalists and had his own idiosyncratic way of pursuing theory. At a recent unveiling of his magnificent bronze bust in the Cavendish Laboratory (June 2000), Malcolm Longair quoted Mott’s own words about himself: “I am neither an experimentalist nor a real mathematician – my theory stops at Schrödinger’s equation. What I have done in this subject is to look at the evidence, do calculations on the back of an envelope and say to the theoretician: ‘If you apply your techniques to this problem, this is how it will come out.’ And to the experimentalist, just the same thing.” And, Longair concluded, Mott’s work epitomises the very best of the Cavendish tradition. A series of short memoirs of Mott are assembled in a book (Davis 1998).

3.3.2 Statistical mechanics

It is one of the wonders of the history of physics that a rigorous theory of the behaviour of a chaotic assembly of molecules – a gas – preceded by several decades the experimental uncovering of the structure of regular, crystalline solids. Attempts to create a kinetic theory of gases go all the way back to the Swiss mathematician, Daniel Bernouilli, in 1738, followed by John Herapath in 1820 and John James Waterston in 1845. But it fell to the great James Clerk Maxwell in the 1860s to take

the first accurate steps – and they were giant steps – in interpreting the pressure–volume–temperature relationship of a gas in terms of a probabilistic (or statistical) analysis of the behaviour of very large populations of mutually colliding molecules – the *kinetic theory of gases*. He was the first to recognise that the molecules would *not* all have the same kinetic energy. The *Maxwell distribution* of kinetic energies of such a population has made his name immortal... even if it had not been immortalised by his electromagnetic equations. The science he created is sometimes called *statistical mechanics*, sometimes *statistical thermodynamics*.

For many years this kind of theory was applied to fluids of various kinds, and it became interestingly applicable to solids much later, in 1925, when W. Lenz in Germany, together with his student Ising, created the theory of *critical phenomena*, which covers phenomena in solids such as ferromagnetism and order–disorder transitions. This important field of theory, which has no proper name even today, has become a major domain of research in its own right and has been recognised with a Nobel Prize awarded to Kenneth Wilson in 1982. The issue was whether an array of spins attached to atoms in a regular array would automatically generate spin alignment and ferromagnetism. Ising only managed a theory in one dimension and wrongly surmised that in higher dimensions there would be no ferromagnetism. The many attempts to generalise the theory to two or three dimensions began with Rudolf Peierls in 1936; he showed that Ising's surmise was wrong.

A population of theorists floating uneasily between physics and materials science (but a number of them working in materials science departments) have become specialists in the statistical thermodynamics of solids, critical phenomena in particular, working in specific fields such as order-disorder transitions; to go into any details of critical phenomena here would take us much too far into the domain of mathematical physics. Two splendid historical accounts of the whole field are by Domb (1995, 1996); another important historical treatment is by Brush (1967). It is intriguing that Ising's name was immortalised in the Ising Model, but in Domb's opinion (private communication), "Ising was a low-grade scientist who by a quirk of fate managed to get his name on thousands of papers, many of them outstandingly good. His own contributions to the field were negligible." Naming of phenomena sometimes rewards the wrong person!

From the historical point of view, an interesting dispute concerns the relative claims of Maxwell in England, Josiah Willard Gibbs in America and Ludwig Boltzmann in Austria to be regarded as the true father of statistical thermodynamics – as distinct from macroscopic chemical thermodynamics, where Gibbs' claims are undisputed. Gibbs' claim rests on a book in 1902 (Gibbs 1902), but this is a good deal later than the various classic papers by Boltzmann. The most important of these were his study of the process by which a gas, initially out of equilibrium, approaches the Maxwell–Boltzmann distribution (as it has since become known), and his

profound investigation in 1877 of the probabilistic basis of entropy, culminating in the relation $S = k \log W$, where S is entropy and W is the probability of a microstate; this immortal equation is carved on Boltzmann's tomb. It is Boltzmann's work which has really made possible the modern flowering of statistical thermodynamics of solids.

The sequence of events is traced with historical precision in a new biography of Boltzmann (Cercignani 1998). An entire chapter (7) is devoted to the Gibbs/Boltzmann connection, culminating in a section entitled "Why is statistical mechanics usually attributed to Gibbs and not to Boltzmann?". Cercignani attributes this to the unfamiliarity of many physicists early in this century with Boltzmann's papers, partly because of the obscurity of his German style (but Gibbs is not easy to read, either!), and partly because the great opinion-formers of early 20th-century physics, Bohr and Einstein, knew little of Boltzmann's work and were inclined to decry it. The circumstances exemplify how difficult it can be to allocate credit appropriately in the history of science.

3.3.3 Magnetism

The study of the multifarious magnetic properties of solids, followed in due course by the sophisticated control of those properties, has for a century been a central concern both of physicists and of materials scientists. The history of magnetism illustrates several features of modern materials science.

That precocious Cambridge engineer, Alfred Ewing, whom we have already met as the adviser of the young Walter Rosenhain, was probably the first to reflect seriously (Ewing 1890) about the origin of ferromagnetism, i.e., the characteristics of strong permanent magnets. He recognised the possibility that the individual magnetic moments presumed to be associated with each constituent atom in a solid somehow kept each other aligned, and he undertook a series of experiments with a lattice of magnetised needles that demonstrated that such an interaction could indeed take place. This must have been one of the first mechanical simulations of a physical process, and these became increasingly popular until eventually they were displaced by computer simulations (Chapter 12). Ewing also did precocious work in the 1880s on the nature of (ferro)magnetic hysteresis, and indeed he invented the term *hysteresis*, deriving from the Greek for 'to be late'.

The central mystery about lodestones and magnetised needles for compasses was where the strong magnetism (what today we call *ferromagnetism*) comes from... what is the basis for all magnetic behaviour? The first written source about the behaviour of (natural) lodestones was written in 1269, and in 1600 William Gilbert (1544–1603) published a notable classic, *De magnete, magnetisque corporibus, et de magno magnete tellure* ...the last phrase referring to 'the great magnet, the earth'. One

biographer says of this: "It is a remarkably 'modern' work – rigorously experimental, emphasising observation, and rejecting as unproved many popular beliefs about magnetism, such as the supposed ability of diamond to magnetise iron. He showed that a compass needle was subject to magnetic dip (pointing downward) and, reasoning from experiments with a spherical lodestone, explained this by concluding that the earth acts as a bar magnet. ... The book... was very influential in the creation of the new mechanical view of science" (Daintith *et al.* 1994). Ever since, the study of magnetism has acted as a link between sciences.

Early in the 20th century, attention was focused on diamagnetic and paramagnetic materials (the great majority of elements and compounds); I do not discuss this here for lack of space. The man who ushered in the modern study of magnetism was Pierre Weiss (1865–1940); he in effect returned to the ideas of Ewing and conceived the notion of a 'molecular field' which causes the individual atomic magnets, the existence of which he felt was inescapable, to align with each other and in this way the feeble magnetisation of each atomic magnet is magnified and becomes macroscopically evident (Weiss 1907). The way Weiss's brilliant idea is put in one excellent historical overview of magnetics research (Keith and Quédec 1992) is: "The interactions within a ferromagnetic substance combine to give the same effects as a fictional mean field..."; such fictional mean fields subsequently became very common devices in the theory of solids. However, the purely magnetic interaction between neighbouring atomic minimagnets was clearly not large enough to explain the creation of the fictional field.

The next crucial step was taken by Heisenberg when he showed in 1928 that the cause of ferromagnetism lies in the quantum-mechanical exchange interaction between electrons imposed by the Pauli exclusion principle; this exchange interaction acts between neighbouring atoms in a crystal lattice. This still left the puzzle of where the individual atoms acquired their magnetic moments, bearing in mind that the crucial component of these moments resides in the *unbalanced* spins of populations of individual electrons. It is interesting here to cite the words of Hume-Rothery, taken from another of his influential books of popularization, *Atomic Theory for Students of Metallurgy* (Hume-Rothery 1946): "The electrons at absolute zero occupy the $N/2$ lowest energy states, each state containing two electrons of opposite spins. Since each electron state cannot contain more than one electron of a given spin, it is clear that any preponderance of electrons of a given spin must increase the Fermi energy, and ferromagnetism can only exist if some other factor lowers the energy." He goes on to emphasize the central role of Heisenberg's exchange energy, which has the final effect of stabilising energy bands containing unequal numbers of positive and negative spin vectors. In 1946 it was also a sufficient approximation to say that the *sign* of the exchange energy depended on the separation of neighbouring atoms, and if that separation was too small, ferromagnetism (with parallel atomic

moments) was impossible and, instead, neighbouring atomic moments were aligned antiparallel, creating *antiferromagnetism*. This phenomenon was predicted for manganese in 1936 by a remarkable physicist, Louis Néel (1904–2000), Pierre Weiss's star pupil, in spite of his self-confessed neglect of quantum mechanics. (His portrait is shown in Chapter 7, Figure 7.8.) There was then no direct way of proving the reality of such antiparallel arrays of atomic moments, but later it became possible to establish the arrangements of atomic spins by neutron diffraction and many antiferromagnets were then discovered. Néel went on to become one of the most influential workers in the broad field of magnetism; he ploughed his own idiosyncratic furrow and it became very fertile (see 'Magnetism as seen by Néel' in Keith and Quédec's book chapter, p. 394). One proof of the importance of interatomic distance in determining whether atomic moments were aligned parallel or antiparallel was the accidental discovery in 1889 of the Heusler alloy, Cu_2MnAl , which was ferromagnetic though none of its constituent elements was thought to be magnetic (the antiferromagnetism of manganese was unknown at the time). This alloy occasioned widespread curiosity long before its behaviour was understood. Thus, the American physicist Robert Wood wrote about it to Lord Rayleigh in 1904: "I secured a small amount in Berlin a few days ago and enclose a sample. Try the filings with a magnet. I suppose the al. and cu. in some way loosen up the manganese molecules so that they can turn around" (Reingold and Reingold 1981); he was not so far out! In 1934 it was found that this phase underwent an order–disorder transition, and that the ordered form was ferromagnetic while the disordered form was apparently non-magnetic (actually, it turned out later, antiferromagnetic). In the ordered form, the distance between nearest-neighbour manganese atoms in the crystal structure was greater than the mean distance was in the disordered form, and this brought about the ferromagnetism. The intriguing story is outlined by Cahn (1998).

The inversion from ferromagnetic to antiferromagnetic interaction between neighbouring atoms is expressed by the "Néel–Slater curve", which plots magnitude and sign of interaction against atomic separation. This curve is itself being subjected to criticism as some experimental observations inconsistent with the curve are beginning to be reported (e.g., Schobinger-Papamantellos *et al.* 1998). In physics and materials science alike, simple concepts tend to be replaced by increasingly complicated ones.

The nature of the exchange energy, and just how unbalanced spin systems become stabilised, was studied more deeply after Hume-Rothery had written, and a very clear non-mathematical exposition of the present position can be found in (Cottrell 1988, p. 101).

The reader interested in this kind of magnetic theory can find some historical memories in an overview by the American physicist, Anderson (1979).

Up to this point, I have treated only the fundamental quantum physics underlying the existence of ferromagnetism. This kind of theory was complemented by the application of statistical mechanics to the understanding of the progressive misalignment of atomic moments as the temperature is raised – a body of theory which led Bragg and Williams to their related mean-field theory of the progressive loss of atomic order in superlattices as they are heated, which we have already met. Indeed, the interconnection between changes in atomic order and magnetic order (i.e., ferromagnetism) is a lively subspeciality in magnetic research; a few permanent magnet materials have superlattices.

Quite separate and distinct from this kind of science was the large body of research, both experimental and theoretical, which can be denoted by the term *technical magnetism*. Indeed, I think it is fair to say that no other major branch of materials science evinces so deep a split between its fundamental and technical branches. Perhaps it would be more accurate to say that the quantum- and statistical-mechanical aspects have become so ethereal that they are of no real concern even to sophisticated materials scientists, while most fundamental physicists (Néel is an exception) have little interest in the many technical issues; their response is like Pauli's.

When Weiss dreamt up his molecular-field model of ferromagnetism, he was at once faced by the need to explain why a piece of iron becomes progressively more strongly magnetised when placed in a gradually increasing energising magnetic field. He realized that this could only be explained by two linked hypotheses: first, that the atomic moments line up along specific crystal directions (a link between the lattice and magnetism), and second, that a crystal must be split into *domains*, each of which is magnetised along a different, crystallographically equivalent, vector... e.g., (1 0 0), (0 1 0) or (0 0 1), each in either a positive or negative direction of magnetisation. In the absence of an energising field, these domains cancel each other out macroscopically and the crystal has no resultant magnetic moment. The stages of Ewing's hysteresis cycle involve the migration of domain boundaries so that some domains (magnetised nearly parallel to the external field) grow larger and 'unfavourable' ones disappear. The alternative mechanism, of the bodily rotation of atomic moments as a group, requires much larger energy input and is hard to achieve.

Domain theory was the beginning of what I call technical magnetism; it had made some progress by the time domains were actually observed in the laboratory. There was then a long period during which the relation between two-phase microstructures in alloys and the 'coercive field' required to destroy macroscopic magnetisation in a material was found to be linked in complex ways to the pinning of domain boundaries by dispersed phases and, more specifically, by local strain fields created by such phases. This was closely linked to the improvement of permanent magnet materials, also known as 'hard' magnets. The terms 'hard' and 'soft' in this context

point up the close parallel between the movement of dislocations and of domain boundaries through local strain fields in crystals.

The intimate interplay between the practitioners of microstructural and phase-diagram research on the one hand, and those whose business it was to improve both soft and hard magnetic materials can be illustrated by many case-histories; to pick just one example, some years ago Fe–Cr–Co alloys were being investigated in order to create improved permanent magnet materials which should also be ductile. Thermodynamic computation of the phase diagram uncovered a miscibility gap in the ternary phase diagram and, according to a brief account (Anon. 1982), “Homma *et al.* experimentally confirmed the existence of a ridge region of the miscibility gap and found that thermomagnetic treatment in the ridge region is effective in aligning and elongating the ferromagnetic particles parallel to the applied magnetic field direction, resulting in a remarkable improvement of the magnetic properties of the alloys”. This sentence refers to two further themes of research in technical magnetism: the role of the shape and dimensions of a magnetic particle in determining its magnetic properties, and the mastery of heat-treatment of alloys in a magnetic field.

A separate study was the improvement of magnetic permeability in ‘soft’ alloys such as are used in transformers and motors by lining up the orientations of individual crystal grains, also known as a preferred orientation; this became an important subspeciality in the design of transformer laminations made of dilute Fe–Si alloys, introduced more than 100 years ago and still widely used.

Another recent success story in technical magnetism is the discovery around 1970 that a metallic glass can be ferromagnetic in spite of the absence of a crystal lattice; but that very fact makes a metallic glass a very ‘soft’ magnetic material, easy to magnetise and thus very suitable for transformer laminations. In recent years this has become a major market. Another success story is the discovery and intense development, during the past decade, of compounds involving rare earth metals, especially samarium and neodymium, to make extraordinarily powerful permanent magnets (Kirchmayr 1996). Going further back in time, the discovery during the last War, in the Philips laboratories in the Netherlands, of magnetic ‘ferrites’ (complex oxides including iron), a development especially associated with the name of the Dutch physicist Snoek, has had major industrial consequences, not least for the growth of tape-recorders for sound and vision which use powders of such materials. These materials are *ferrimagnetic*, an intriguing halfway house between ferromagnetic and antiferromagnetic materials: here, the total magnetic moments of the two families of atoms magnetised in opposing directions are unequal, leaving a macroscopic balance of magnetisation. The ferrites were the first insulating magnetic materials to find major industrial use (see Section 7.3).

This last episode points to the major role, for a period, of industrial laboratories such as the giant Philips (Netherlands), GE (USA) and Siemens (Germany)

laboratories in magnetic research, a role very clearly set out in the book chapter by Keith and Quédec. GE, for instance, in the 1950s developed a family of permanent magnets exploiting the properties of small, elongated magnetic particles. Probably the first laboratory to become involved in research on the fringes of magnetism was the Imphy laboratory in France at the end of the nineteenth century: a Swiss metallurgist named Charles-Edouard Guillaume (1861–1938), working in Paris, had in 1896 discovered an iron–nickel alloy which had effectively zero coefficient of thermal expansion near room temperature, and eventually (with the support of the Imphy organisation) tracked this down to a loss of ferromagnetism near room temperature, which entails a ‘magnetostrictive’ contraction that just compensates the normal thermal expansion. This led to a remarkable programme of development in what came to be known as ‘precision metallurgy’ and products, ‘Invar’ and ‘Elinvar’, which are still manufactured on a large scale today and are, for instance, essential components of colour television tubes. Guillaume won the Nobel Prize for Physics in 1920, the only such prize ever to be awarded for a metallurgical achievement. The story is told in full detail in a centenary volume (Béranger *et al.* 1996).

Most recently, industrial magnetics research has taken an enormous upswing because of the central importance of magnetic recording in computer memories. Audio-recording on coated tape was perfected well before computer memories came on the scene: the first step (1900) was recording on iron wires, while plastic recording tape coated with iron oxide was developed in Germany during the First World War. Magnetic computer memories, old and new, are treated in Section 7.4. Not all the innovations here have been successful: for instance, the introduction of so-called ‘bubble memories’ (with isolated domains which could be nudged from one site to a neighbouring one to denote a bit of memory) (Wernick and Chin 1992) failed because they were too expensive. However, a remarkable success story, to balance this, is the magnetoresistant multilayer thin film. This apparently emerged from work done in Néel’s Grenoble laboratory in the 1960s: thin films of a ferromagnet and an antiferromagnet in contact acquire a new kind of magnetic anisotropy from exchange coupling (à la Heisenberg) and this in turn was found to cause an unusually large change of electrical resistivity when a magnetic field is applied normal to the film (a phenomenon known as magnetoresistivity). This change in resistivity can be used to embody an electronic signal to be recorded. The matter languished for a number of years and around 1978 was taken up again. Multilayers such as Co–Pt are now used on a huge scale as magnetoresistive memories, as is outlined in a survey by Simonds (1995). (See also Section 7.4.) It could be said that this kind of development has once again brought about a rapprochement between the quantum theorists and the hard-headed practical scientist.

Not only information technology has benefited from research in technical magnetism. Both permanent magnets and electromagnets have acquired manifold

uses in industry; thus automotive engines nowadays incorporate ever more numerous permanent magnets. An unexpected application of magnets of both kinds is to magnetic bearings, in which a rotating component is levitated out of contact with an array of magnets under automatic control, so that friction-free operation is achieved. As I write this, the seventh international symposium on magnetic bearings is being planned in Zurich. The ultracentrifuges which played such an important part in determining molecular weights of polymers (see Chapter 8, Section 8.7) rely on such magnetic bearings.

Magnetism intrudes in the most unexpected places. A very recent innovation is the use of 'magnetorheological finishing'. An American company, QED Technologies in Rochester, NY, has developed a polishing agent, a slurry of carbonyl iron, cerium oxide (a hard abrasive) and other materials. A magnetic field converts this slurry from a mobile liquid to a rigid solid. Thus a coating of the slurry can take up the shape of a rough object to be polished and then 'solidified' to accelerate polishing without use of a countershape. This is useful, for instance, in polishing aspheric lenses.

The literature of magnetism research, both in journals and in books, is huge, and a number of important titles help in gaining a historical perspective. A major classic is the large book (Bozorth 1951), simply called *Ferromagnetism*, by Richard Bozorth (1896–1981). An English book, more angled towards fundamental themes, is by Bates (1961). An excellent perspective on the links between metallurgy and magnetism is offered by an expert on permanent magnets, Kurt Hoselitz (1952), also by one of the seminar volumes formerly published by the American Society for Metals (ASM 1959), a volume which goes in depth into such arcane matters as the theory of the effects caused by annealing alloys in a magnetic field. An early, famous book which, precociously, strikes a judicious balance between fundamental physics and technical considerations, is by Becker and Döring (1939), also simply called *Ferromagnetismus*. An excellent perspective on the gradually developing ideas of technological (mostly industrial) research on ferromagnetic materials can be garnered from two survey papers by Jacobs (1969, 1979), the second one being subtitled "a quarter-century overview". An early overview of research in technical magnetism, with a British slant, is by Sucksmith (1949).

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Chapter 4

The Virtues of Subsidiarity

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Chapter 4

The Virtues of Subsidiarity

4.1. THE ROLE OF PAREPISTEMES IN MATERIALS SCIENCE

Physical metallurgy, like other sciences and technologies, has its mainline topics: examples, heat transfer in mechanical engineering, distillation theory in chemical engineering, statistical mechanics in physics, phase transformations in physical metallurgy. But just as one patriarch after a couple of generations can have scores of offspring, so mainline topics spawn subsidiary ones. The health of any science or technology is directly dependent on the vigour of research on these subsidiary topics. This is so obvious that it hardly warrants saying... except that 200 years ago, hardly anyone recognised this truth. The ridiculous doctrine of yesteryear has become the truism of today.

What word should we use to denote such subsidiary topics? All sorts of dry descriptors are to hand, such as ‘subfield’, ‘subdiscipline’, ‘speciality’, ‘subsidiary topic’, but they do not really underline the importance of the concept in analysing the progress of materials science. So, I propose to introduce a neologism, suggested by a classicist colleague in Cambridge: *parepisteme*. This term derives from the ancient Greek ‘episteme’ (a domain of knowledge, a science... hence ‘epistemology’), plus ‘par(a)-’, a prefix which among many other meanings signifies ‘subsidiary’. The term *parepisteme* can be smoothly rendered into other Western languages, just as Greek- or Latin-derived words like entropy, energy, ion, scientist have been; and another requirement of a new scientific term, that it can be turned into an adjective (like ‘energetic’, ‘ionic’, etc.) is also satisfied by my proposed word... ‘parepistemic’.

A striking example of the importance of narrowing the focus in research, which is what the concept of the *parepisteme* really implies, is the episode (retailed in Chapter 3, Section 3.1.1) of Eilhard Mitscherlich’s research, in 1818, on the crystal forms of potassium phosphate and potassium arsenate, which led him, quite unexpectedly, to the discovery of isomorphism in crystal species and that, in turn, provided heavyweight evidence in favour of the then disputed atomic hypothesis. As so often happens, the general insight comes from the highly specific observation.

Some *parepistemes* are pursued by small worldwide groups whose members all know each other, others involve vast communities which, to preserve their sanity, need to sub-classify themselves into numerous subsets. They all seem to share the feature, however, that they are not disciplines in the sense that I have analysed these

in Chapter 2: although they all form components of degree courses, none of the parepistemes in materials science that I exemplify below are degree subjects at universities – not even crystallography, huge field though it is.

The essence of the concept of a parepisteme, to me, is that parepistemic research is *not* directly aimed at solving a practical problem. Ambivalent views about the justifiability of devoting effort to such research can be found in all sciences. Thus a recent overview of a research programme on the genome of a small worm, *C. elegans* (the first animal genome to be completely sequenced) which was successfully concluded after an intense 8-year effort (Pennisi 1998), discusses some reactions to this epoch-making project. Many did not think it would be useful to spend millions of dollars “on something which didn’t solve biological problems right off”, according to one participant. Another, commenting on the genetic spinoffs, remarked that “suddenly you have not just your gene, but context revealed. You’re looking at the forest, not just the tree.” Looking at the forest, not just the tree – that is the value of parepistemic research in any field.

A good way of demonstrating the importance of parepistemes, or in other terms, the virtues of subsidiarity, is to pick and analyse just a few examples, out of the many hundreds which could be chosen in the broad field of materials science and engineering.

4.2. SOME PAREPISTEMES

4.2.1 *Metallic single crystals*

As we saw in Section 3.1.3, Walter Rosenhain in 1900 published convincing micrographic evidence that metals are assemblies of individual crystal grains, and that plastic deformation of a metal proceeds by slip along defined planes in each grain. It took another two decades before anyone thought seriously of converting a piece of metal into a *single crystal*, so that the crystallography of this slip process could be studied as a phenomenon in its own right. There would, in fact, have been little point in doing so until it had become possible to determine the crystallographic orientation of such a crystal, and to do that with certainty required the use of X-ray diffraction. That was discovered only in 1912, and the new technique was quite slow in spreading across the world of science. So it is not surprising that the idea of growing metallic single crystals was only taken seriously around the end of World War I.

Stephen Keith, a historian of science, has examined the development of this parepisteme (Keith 1998), complete with the stops and starts caused by fierce competition between individuals and the discouragement of some of them, while a shorter account of the evolution of crystal-growing skill can be found in the first

chapter of a book by one of the early participants (Elam 1935). There are two approaches to the problem: one is the ‘critical strain-anneal’ approach, the other, crystal growth from the melt.

The strain-anneal approach came first chronologically, apparently because it emerged from the chance observation, late in the 19th century, of a few large grains in steel objects. This was recognised as being deleterious to properties, and so some research was done, particularly by the great American metallurgist Albert Sauveur, on ways of *avoiding* the formation of large grains, especially in iron and steel. In 1912, Sauveur published the finding that large grains are formed when initially strain-free iron is given a *small* (critical) strain and subsequently annealed: the deformed metal recrystallises, forming just a few large new grains. If the strain is smaller than the critical amount, there is no recrystallisation at all; if it is larger, then many grains are formed and so they are small. This can be seen in Figure 4.1, taken from a classic ‘metallographic atlas’ (Hanemann and Schrader 1927) and following on an observation recorded by Henri Le Chatelier in France in 1911: A hardened steel ball was impressed into the surface of a piece of mild steel, which was then annealed; the further from the impression, the smaller the local strain and the larger the resultant grains, and the existence of a critical strain value is also manifest. This critical-strain method, using tensile strain, was used in due course for making large iron crystals (Edwards and Pfeil 1924) – in fact, because of the allotropic transformations during cooling of iron from its melting-point, no other method would have worked for iron – but first came the production of large aluminium crystals.

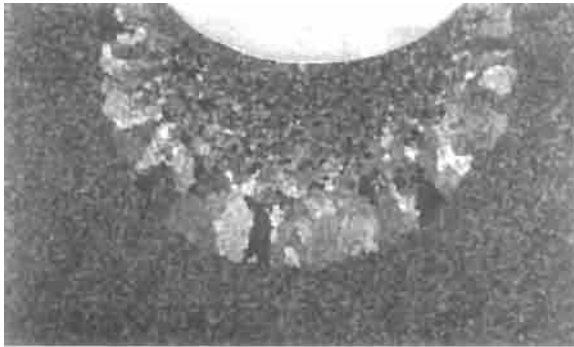


Figure 4.1. Wrought low-carbon mild steel, annealed and impressed by a Brinell ball (12 mm diameter), then annealed 30 min at 750°C and sectioned. The grain size is largest just inside the zone beyond which the critical strain for recrystallisation has not quite been attained (after Hanemann and Schrader 1927, courtesy M. Hillert).

The history of the researches that led to large aluminium crystals is somewhat confused, and Keith has gone into the sequence of events in some detail. Probably the first relevant publication was by an American, Robert Anderson, in 1918; he reported the effects of strain preceding annealing (Anderson 1918). My late father-in-law, Daniel Hanson (1892–1953), was working with Rosenhain in the National Physical Laboratory near London during World War I, and told me that he had made the first aluminium crystals at that time; but the circumstances precluded immediate publication. I inherited two of the crystals (over 100 cm³ in size) and presented them to the Science Museum in London; Jane Bowen of that Museum (Bowen 1981) undertook some archival research and concluded that Hanson may indeed have made the first crystals around the end of the War. Another early ‘player’ was Richard Seligman, then working in H.C.H. Carpenter’s department of metallurgy at Imperial College. Seligman became discouraged for some reason, though not until he had stated in print that he was working on making single crystals of aluminium, in consultation with Rosenhain. (Clearly he loved the metal, for later he founded a famous enterprise, the Aluminium Plant and Vessel Company.) It appears that when Carpenter heard of Hanson’s unpublished success, he revived Seligman’s research programme, and jointly with Miss Constance Elam, he published in 1921 the first paper on the preparation of large metal crystals by the strain-anneal method, and their tensile properties (Carpenter and Elam 1921). Soon, aluminium crystals made in this way were used to study the changes brought about by fatigue testing (Gough *et al.* 1928), and a little later, Hanson used similar crystals to study creep mechanisms.

The other method of growing large metal crystals is controlled freezing from the melt. Two physicists, B.B. Baker and E.N. da C. Andrade, in 1913–1914 published studies of plastic deformation in sodium, potassium and mercury crystals made from the melt. The key paper however was one by a Pole, Jan Czochralski (1917), who dipped a cold glass tube or cylinder into a pan of molten Pb, Sn or Zn and slowly and steadily withdrew the crystal which initially formed at the dipping point, making a long single-crystal cylinder when the kinetics of the process had been judged right. Czochralski’s name is enshrined in the complex current process, based on his discovery, for growing huge silicon crystals for the manufacture of integrated circuits.

Probably the first to take up this technique for purposes of scientific research was Michael Polanyi (1891–1976) who in 1922–1923, with the metallurgist Erich Schmid (1896–1983) and the polymer scientist-to-be Hermann Mark (1895–1992), studied the plastic deformation of metal crystals, at the Institute of Fibre Chemistry in Berlin-Dahlem; in those days, good scientists often earned striking freedom to follow their instincts where they led, irrespective of their nominal specialisms or the stated objective of their place of work. In a splendid autobiographical account of those

days, Polanyi (1962) explains how Mark made the Czochralski method work well for tin by covering the melt surface with a mica sheet provided with a small hole. In 1921, Polanyi had used natural rocksalt crystals and fine tungsten crystals extracted from electric lamp filaments to show that metal crystals, on plastic stretching, became work-hardened. The grand old man of German metallurgy, Gustav Tammann, was highly sceptical (he was inclined to be sceptical of everything not done in Göttingen), and this reaction of course spurred the young Polanyi on, and he studied zinc and tin next (Mark *et al.* 1922). Work-hardening was confirmed and accurately measured, and for good measure, Schmid about this time established the law of critical shear stresses for plastic deformation. In Polanyi's own words: "We were lucky in hitting on a problem ripe for solution, big enough to engage our combined faculties, and the solution of which was worth the effort". Just before their paper was out, Carpenter and Robertson published their own paper on aluminium; indeed, the time was ripe. By the end of 1923, Polanyi had moved on to other things (he underwent many intellectual transitions, eventually finishing up as a professor of philosophy in Manchester University), but Erich Schmid never lost his active interest in the plastic deformation of metal crystals, and in 1935, jointly with Walter Boas, he published *Kristallplastizität*, a deeply influential book which assembled the enormous amount of insight into plastic deformation attained since 1921, insight which was entirely conditional on the availability of single metal crystals. "Ripeness" was demonstrated by the fact that *Kristallplastizität* appeared simultaneously with Dr. Elam's book on the same subject. Figure 4.2 shows a medal struck in 1974 to mark the 50th anniversary of Schmid's discovery, as a corollary of the 1922 paper by



Figure 4.2. Medal struck in Austria to commemorate the 50th anniversary of the discovery of the critical shear stress law by Erich Schmid. The image represents a stereographic triangle with 'isobars' showing crystal orientations of constant resolved shear stress (courtesy H.P. Stüwe).

Mark, Polanyi and Schmid, of the constant resolved shear-stress law, which specifies that a crystal begins to deform plastically when the shear stress on the most favoured potential slip plane reaches a critical value.

Aside from Czochralski, the other name always associated with growth of metal crystals from the melt is that of Percy Bridgman (1882–1961), an American physicist who won the Nobel Prize for his extensive researches on high-pressure phenomena (see below). For many of his experiments on physical properties of metals (whether at normal or high pressure) – for instance, on the orientation dependence of thermoelectric properties – he needed single crystals, and in 1925 he published a classic paper on his own method of doing this (Bridgman 1925). He used a metal melt in a glass or quartz ampoule with a constriction, which was slowly lowered through a thermal gradient; the constriction ensured that only one crystal, nucleated at the end of the tube, made its way through into the main chamber. In a later paper (Bridgman 1928) he showed how, by careful positioning of a glass vessel with many bends, he could make crystals of varied orientations. In the 1925 paper he recorded that growing a single crystal from the melt ‘sweeps’ dissolved impurities into the residual melt, so that most of the crystal is purer than the initial melt. He thus foreshadowed by more than 20 years the later discovery of zone-refining.

Metallic monocrystals were not used only to study plastic deformation. One of the more spectacular episodes in single-crystal research was F.W. Young’s celebrated use of spherical copper crystals, at Oak Ridge National Laboratory in America, to examine the anisotropy of oxidation rates on different crystal planes (Young *et al.* 1956). For this purpose, spheres were machined from cylindrical copper crystals, carefully polished by mechanical means and then made highly smooth by anodic electrolytic polishing, thereby removing all the surface damage that was unavoidably caused by mechanical polishing. Figure 4.3 shows the optical interference patterns on such a crystal after oxidation in air, clearly showing the cubic symmetry of the crystal. Such patterns were used to study the oxidation kinetics on different crystal faces, for comparison with the then current theory of oxidation kinetics. Most of Young’s extensive researches on copper crystals (1951–1968) concerned the etching of dislocations, but the oxidation study showed how important such crystals could be for other forms of fundamental metallurgical research.

Detailed, critical surveys of the variants and complexities of crystal growth from the melt were published for low-melting metals by Goss (1963) and for high-melting metals (which present much greater difficulties) by Schadler (1963).

It is worth while, now, to analyse the motivation for making metallic single crystals and how, in turn, their production affected physical metallurgy. Initially, metallurgists were concerned to prevent the accidental generation of coarse grains in parts of objects for load-bearing service, and studied recrystallisation with this objective in view. To quote Keith, “Iron crystals... were achieved subsequently by

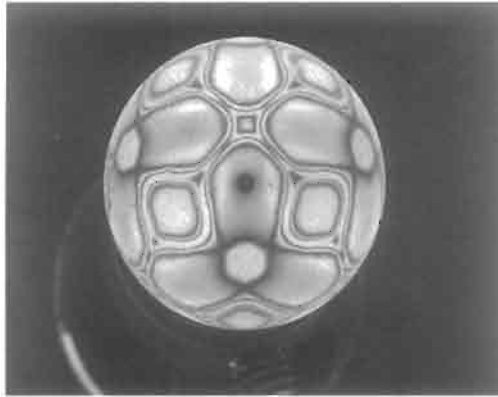


Figure 4.3. Polished spherical copper monocrystal, oxidised to show anisotropy of oxidation rates (after Young *et al.* 1956).

Edwards and Pfeil on the back of investigations... motivated initially by the commercial importance of avoiding coarse recrystallisation in metals during manufacturing processes”. Then, a few foreseeing metallurgists like Hanson (1924) and Honda (1924) saw the latent possibilities for fundamental research; thus Hanson remarked: “It (the production of metal crystals) opened up the possibility of the study of behaviour of metals, and particularly of iron and steel, such as had not presented itself before”. During the 10 years following, this possibility was energetically pursued all over the world. That precocious physicist, Bridgman, saw the same possibilities from a physicist’s perspective. So a *parepisteme* developed, initially almost accidentally, by turning on its head a targeted practical objective, and many novel insights followed.

Growth of nonmetallic crystals developed partly as a purely academic study that led to major insights, such as Charles Frank’s prediction of spiral growth at dislocation sites (Chapter 3, Section 3.2.3.3), and partly as a targeted objective because items such as quartz and ruby crystals were needed for frequency standards, quartz watches, lasers and watch bearings. Some extraordinary single crystals have been grown, including crystals of solid helium grown at $0.1\ \mu\text{m}$ per second at about $1\ \text{K}$ (Schuster *et al.* 1996). Crystal growth has become a very major field with numerous books and several journals (e.g., the massive *Journal of Crystal Growth*), but only for metals did single-crystal growth emerge from an initial desire to avoid large grains.

While for many years, metal single crystals were used only as tools for fundamental research, at the beginning of the 1970s single-crystal gas-turbine blades began to be made in the hope of improving creep performance, and today all such blades are routinely manufactured in this form (Duhl 1989).

4.2.2 Diffusion

The migration of one atomic species in another, in the solid state, is the archetype of a materials-science parepisteme. From small beginnings, just over a century ago, the topic has become central to many aspects of solid-state science, with a huge dedicated literature of its own and specialised conferences attended by several hundred participants.

A recent historian of diffusion, Barr (1997), has rediscovered a precociously early study of solid-state diffusion, by the 17th-century natural philosopher, Robert Boyle, (1684); Boyle was one of those men who, in Restoration England, were described as ‘the curious’. He describes several experiments involving copper and several other elements and goes on to say: “...there is a way, by which, without the help of salts sulphur or arsenic, one may make a solid and heavy body soak into the pores of that metal and give it a durable colour. I shall not mention the way, because of the bad use that may be made of it...” Barr concludes, from internal evidence, that Boyle had diffused zinc into copper and preceded by fifty years the discovery, in 1732, by Christopher Pinchbeck of the Cu–Zn alloy later called ‘pinchbeck’ and used as a cheap substitute for gold. Boyle was clearly worried that his experiment, if fully described, might clear the way for forgery of apparent gold coins. Boyle verified that the zinc really had penetrated deeply into the copper (without the copper having been melted), by filing a cross-section and examining it. Boyle’s findings were promptly forgotten for over 300 years... the time was not ripe for them. It is ironic, however, that this first attempt to examine solid-state diffusion was partly suppressed precisely because it was too practical.

The next historical waystop is the research of Thomas Graham, also in England, whom we have already encountered (Section 2.1.4) as the originator of colloid science, and again in Section 3.1.1, described as “the leading atomist of his age”. In the 1830s (Graham 1833) he studied the diffusion of various gases into air through a porous plug that slowed down the motion of gas molecules, and found that the rate of motion of a gas is linked to its molecular weight. This was the first attempt at a quantitative study of diffusion, albeit not in a solid. Graham’s researches were perhaps the first to indicate that the then standard static lattice model of a gas (according to which the gas molecules are arranged on a very dilute lattice subject to mutual repulsion of the molecules... see Mendoza 1990) needed to be replaced by a dynamic model in which all the molecules are in ceaseless motion. Later on, Thomas studied diffusion of solutes in liquids.

Next, the German Adolph Fick (1829–1901), stimulated by Graham’s researches, sought to turn diffusion into a properly quantitative concept and formulated the law named after him, relating the rate of diffusion to the steepness of the concentration gradient (Fick 1855), and confirmed his law by measurements of diffusion in liquids. In a critical examination of the influence of this celebrated piece of theory, Tyrrell

(1964) opined that the great merit of Fick's work lay in the stimulus it has given for over a century to *accurate* experimental work in the field, and goes on to remark: "A glance at Graham's extensive, and almost unreadable, descriptions of quantitative studies on diffusion, will show how great a contribution it (Fick's work) was".

All the foregoing were precursors to the first accurate research on diffusion in *solids*, which was performed by William Roberts-Austen (1843–1902), who spent his working life in London (Figure 4.4). It has been said that Graham's greatest contribution to science was to employ Roberts-Austen as his personal assistant at the London Mint (a factory for producing coinage), where he became a skilled assayer, learning to analyse metal concentrations quantitatively. Roberts-Austen, an immensely hard worker, not only became immortal for his researches on diffusion but also played a major role in the introduction of binary metallic phase diagrams; thus in 1897 he presented the first *T-concentration* diagram for Fe–C, which the Dutchman Roozeboom (Section 3.1.2) soon after turned into a proper phase diagram. The face-centred cubic form of iron, *austenite*, was in due course named after Roberts-Austen (there is no phase with a double-barrelled name!). This aspect of his distinguished career, as also features of his life, are outlined in a recent review (Kayser and Patterson 1998). His work on diffusion is discussed by Barr (1997) and



Figure 4.4. W. Roberts-Austen (courtesy of M. McLean, Imperial College, London).

also in a lively manner by Koiwa (1998), who further discusses Fick's career in some detail.

In his classic paper on solid-state diffusion (Roberts-Austen 1896a), he remarks that "my long connection with Graham's researches made it almost a duty to attempt to extend his work on liquid diffusion to metals". He goes on to say that initially he abandoned this work because he had no means of measuring high temperatures accurately. This same problem was solved at about the same time by Heycock and Neville (Section 3.1.2) by adopting the then novel platinum-resistance thermometer; Roberts-Austen in due course made use of Le Chatelier's platinum/platinum-rhodium thermocouple, combined with his own instrument for recording temperature as a function of time. His researches on solid-state diffusion became feasible for three reasons: the concept was instilled in his mind by his mentor, Graham; the theoretical basis for analysing his findings had been provided by Fick; and the needful accuracy in temperature came from instrumental improvements. All three... stimulus, theory, instruments... are needed for a major advance in experimental research.

Roberts-Austen's research was focused primarily on the diffusion of gold in solid lead, a fortunate choice, since this is a fast-diffusing couple and this made his sectioning measurements easier than they would have been for many other couples. He chose a low-melting solvent because he surmised, correctly, that the melting-temperature played a dominant role in determining diffusivity. About the same time he also published the first penetration profile for carbon diffusing in iron (Roberts-Austen 1896b); indeed, this was the very first paper in the new *Journal of the Iron and Steel Institute*. It is not clear, according to Barr, whether Roberts-Austen recognised that the diffusion kinetics were related exponentially to temperature, in accordance with Arrhenius's concept of activation energy (Section 2.1.1), but by 1922 that linkage had certainly been recognised by Dushman and Langmuir (1922).

Slight experimental departures from the Arrhenius relation in turn led to recognition of anomalous diffusion mechanisms. Indeed, after a gap in activity of a quarter century, in the 1920s, interest veered to the *mechanism(s)* involved in solid-state diffusion. The history of these tortuous discussions, still in progress today, has been told by Tuijn (1997) and also discussed in Koiwa's papers mentioned above. In 1684, Boyle had in passing referred to his solute 'soaking into the pores of copper', and in a way this was the centre of all the debates in the 1920s and 1930s: the issue was whether atoms simply switched lattice sites without the aid of crystal defects, or whether diffusion depends on the presence, and migration, of vacant lattice sites (vacancies) or, alternatively, on the ability of solute atoms to jump off the lattice and into interstitial sites. The history of the point-defect concept has already been outlined (Chapter 3, Section 3.2.3.1), but one important player was only briefly mentioned. This was a Russian, Yakov Frenkel, who in 1924,

while visiting Germany, published a crucial paper (Frenkel 1924). In this he argued that since atoms in a crystal can sublime (evaporate) from the surface, so they should be able to do *inside* the crystal, that is, an atom should be able to wander from its proper site into an interstitial site, creating what has since been termed a ‘Frenkel defect’ (a vacant lattice site *plus* an interstitial atom nearby). He followed this up by a further paper (Frenkel 1926) which Schmalzried, in his important textbook on chemical kinetics of solids, describes as a “most seminal theoretical paper” (Schmalzried 1995). Here he points out that in an ‘ionic’ crystal such as silver bromide, some of the silver ions will ‘evaporate’ into interstitial sites, leaving silver vacancies behind; the two kinds of ion will behave differently, the size being an important variable. Frenkel recognised that point defects are an *equilibrium feature* of a crystal, the concentration being determined by, in Schmalzried’s words, “a compromise between the ordering interaction energy and the entropy contribution of disorder (point defects, in this case)”. In its own way, this was as revolutionary an idea as Willard Gibbs’s original notion of chemical equilibrium in thermodynamic terms.

There is no space here to map the complicated series of researches and sustained debates that eventually led to the firm recognition of the crucial role of crystal vacancies in diffusion, and Tuijn’s brief overview should be consulted for the key events. A key constituent in these debates was the observation in 1947 of the *Kirkendall effect* – the motion of an inert marker, inserted between two metals welded together before a diffusion anneal, relative to the location of the (now diffuse) interface after the anneal. This motion is due to the fact that vacancies in the two metals move at different speeds. The effect was reported by Smigelskas and Kirkendall (1947). It then met the unrelenting scepticism of Kirkendall’s mentor, Robert Mehl (a highly influential metallurgist whom we met in Section 3.2.1), and so took some time to make its full impact. In due course, in 1951, one of Mehl’s later students, Carrea da Silva, himself put the phenomenon beyond doubt, and on his deathbed in 1976, Mehl was reconciled with Kirkendall (who had by then long since left research to become a scientific administrator – the fate of so many fine researchers). This affecting tale is told in detail in a historical note on the Kirkendall effect by Nakajima (1997); it is well worth reading.

In some materials, semiconductors in particular, interstitial atoms play a crucial role in diffusion. Thus, Frank and Turnbull (1956) proposed that copper atoms dissolved in germanium are present both substitutionally (together with vacancies) *and* interstitially, and that the vacancies and interstitial copper atoms diffuse independently. Such diffusion can be very rapid, and this was exploited in preparing the famous micrograph of Figure 3.14 in the preceding chapter. Similarly, it is now recognised that transition metal atoms dissolved in silicon diffuse by a very fast, predominantly interstitial, mechanism (Weber 1988).

Turnbull was also responsible for another insight of great practical importance. In the late 1950s, while working at the General Electric research laboratories during their period of devotion to fundamental research, he and his collaborators (Desorbo *et al.* 1958) were able to explain the fact that Al–Cu alloys quenched to room temperature initially age-harden (a diffusion-linked process) several orders of magnitude faster than extrapolation of measured diffusion rates at high temperatures would have predicted. By ingenious electrical resistivity measurements, leading to clearly defined activation energies, they were able to prove that this disparity was due to excess vacancies ‘frozen’ into the alloy by the high-speed quench from a high temperature. Such quenched-in vacancies are now known to play a role in many metallurgical processes.

Another subsidiary field of study was the effect of high concentrations of a diffusing solute, such as interstitial carbon in iron, in slowing diffusivity (in the case of carbon in fcc austenite) because of mutual repulsion of neighbouring dissolved carbon atoms. By extension, high carbon concentrations can affect the mobility of substitutional solutes (Babu and Bhadeshia 1995). These last two phenomena, quenched-in vacancies and concentration effects, show how a parepisteme can carry smaller parepistemes on its back.

From diffusion of one element in another it is a substantial intellectual step to the study of the diffusion of an element in itself... self-diffusion. At first sight, this concept makes no sense; what can it matter that identical atoms change places in a crystalline solid? In fact, self-diffusion plays a key role in numerous processes of practical consequence, for instance: creep, radiation damage, pore growth, the evolution of microstructure during annealing; the attempts to understand how self-diffusion operates has led to a wider understanding of diffusion generally. To study self-diffusion, some way has to be found to distinguish some atoms of an element from others, and this is done either by using radioactive atoms and measuring radioactivity, or by using stable isotopes and employing mass-spectrometry. The use of radio-isotopes was pioneered by a Hungarian chemist, György von Hevesy (1885–1966): he began in 1921 with natural radio-isotopes which were the end-product of a radioactive decay chain (^{210}Pb and ^{212}Pb), and later moved on to artificial radio-isotopes. As Koiwa (1998) recounts, he was moved to his experiments with lead by his total failure to separate radium D (in fact, as it proved, a lead isotope) from a mass of lead in which the sample had been intentionally embedded. Here, as in the attempts to prevent excessive grain growth in iron, a useful but unexpected concept emerged from a frustrating set of experiments. Later, von Hevesy moved on to other exploits, such as the discovery of the element hafnium.

There is no space here to go into the enormous body of experiment and theory that has emerged from von Hevesy’s initiative. The reader is referred to an excellent critical overview by Seeger (1997). Important concepts such as the random-walk

model for the migration of vacancies, modified by non-random aspects expressed by the 'correlation coefficient', emerged from this work; the mathematics of the random walk find applications in far-distant fields, such as the curling-up of long polymer chains and the elastic behaviour of rubber. (Indeed, the random walk concept has recently been made the basis of an 'interdisciplinary' section in a textbook of materials science (Allen and Thomas 1999).) When it was discovered that some plots of the logarithm of diffusion coefficients against reciprocal temperature were curved, the recognition was forced that divacancies as well as monovacancies can be involved in self-diffusion; all this is set out by Seeger.

The transport of charged ions in alkali halides and, later on, in (insulating) ceramics is a distinct *parepisteme*, because electric fields play a key role. This large field is discussed in Schmalzried's 1995 book, already mentioned, and also in a review by one of the pioneers (Nowick 1984). This kind of study in turn led on to the developments of superionic conductors, in which ions and not electrons carry substantial currents (touched on again in Chapter 11, Section 11.3.1.1).

Diffusion now has its own specialised journal, *Defect and Diffusion Forum*, which published the successive comprehensive international conferences devoted to the *parepisteme*.

Some of the many fields of MSE in which an understanding of, and quantitative knowledge of, diffusion, self-diffusion in particular, plays a major role will be discussed in the next chapter.

4.2.3 High-pressure research

In Section 3.2.5 something was said about the central role of measurements of physical and mechanical properties at high pressures as a means of understanding processes in the interior of the earth. This kind of measurement began early in the 20th century, but in a tentative way because the experimental techniques were unsatisfactory. Pressures were usually generated by hydraulic means but joints were not properly pressure-tight, and there were also difficulties in calibration of pressures. All this was changed through the work of one remarkable man, Percy (known as Peter) Bridgman (1882–1961). He spent his entire career, student, junior researcher and full professor (from 1919) at Harvard University, and although all his life (except during the Wars) he was fiercely devoted to the pursuit of basic research, as an unexpected byproduct he had enormous influence on industrial practice. Good accounts of his career can be found in a biographical memoir prepared for the National Academy of Sciences (Kemble and Birch 1970) and in an intellectual biography (Walter 1990). Figure 4.5 is a portrait. His numerous papers (some 230 on high-pressure research alone) were published in collected form by Harvard University Press in 1964. Two books by Bridgman himself give accounts of his



Figure 4.5. P.W. Bridgman (courtesy of G. Holton, Harvard University).

researches from 1906 onwards. One (Bridgman 1931, 1949) includes a useful historical chapter: here we learn that in the nineteenth century, attention focused largely on the liquefaction of gases and on supercritical behaviour that removed the discontinuity between gaseous and liquid states, whereas early in the twentieth century, attention began to be focused on condensed matter, both liquids and solids, with geological laboratories well to the fore. Bridgman's other relevant book (Bridgman 1952) was devoted entirely to plasticity and fracture in pressurised solids. A very recent book (Hazen 1999) on diamond synthesis includes an excellent chapter on *The legacy of Percy Bridgman*.

Bridgman came to high-pressure research through a project to check the predicted relationship between the density of a glass of specified composition and its refractive index. He quickly became so fascinated by the technical problems of creating high pressures while allowing measurements of properties to be made that he focused on this and forgot about refractive indices. (This sort of transfer of attention is how a variety of parastatements were born.) Bridgman was an excellent mechanic who did not allow professional craftsmen into his own home – his memoirists refer to his “fertile mechanical imagination and exceptional manipulative

dexterity” – and he quickly designed a pressure seal which became the tighter, the greater the pressure on it; the Bridgman seal solved the greatest problem in high-pressure research. He also learned enough metallurgy to select appropriate high-strength steels for the components of his apparatus. He had few research students and did most of his research with his own hands. (It is said of him that when news of his Nobel Prize came through in 1946, a student sought to interrupt him during a period of taking experimental readings to tell him the news but was told to go away and tell him the details later.) Once his apparatus worked well, he focused on electrical properties for preference, especially of single crystals (see Section 4.2.1) but became so interested by the occasional distortions and fractures of his equipment that he undertook extensive research on enhanced plastic deformability of metals and minerals, some of them normally completely brittle, under superimposed hydrostatic pressure; he undertook research for the US armed forces on this theme that led to several important military applications, and eventually he wrote the aforementioned book dedicated to this (Bridgman 1952). These researches cleared the path for much subsequent research in geological laboratories.

Bridgman had strong views on the importance of empirical research, influenced as little as possible by theory, and this helped him test the influence of numerous variables that lesser mortals failed to heed. He kept clear of quantum mechanics and dislocation theory, for instance. He became deeply ensconced in the philosophy of physics research; for instance, he published a famous book on dimensional analysis, and another on ‘the logic of modern physics’. When he sought to extrapolate his ideas into the domain of social science, he found himself embroiled in harsh disputes; this has happened to a number of eminent scientists, for instance, J.D. Bernal. Walter’s book goes into this aspect of Bridgman’s life in detail.

It is noteworthy that though Bridgman set out to undertake strictly fundamental research, in fact his work led to a number of important industrial advances. Thus his researches on mechanical properties led directly to the development of high-pressure metal forming in industry: the story of this is told by Frey and Goldman (of the Ford Motor Company) (1967). Thus, copper at the relatively low hydrostatic pressure of 100 000 psi (0.7 GPa) can be deformed to enormous strains without fracture or reannealing, and connectors of complex shape can be cold-formed in a single operation. Frey and Goldman claim that their development programme proved “exceedingly profitable”, and they directly credit Bridgman for its genesis.

In the same volume, two former research directors of the GE Corporate Research Center (Suits and Bueche 1967) record the case-history of GE’s ‘diamond factory’. The prolonged research effort began in 1941 with a contract awarded to Bridgman; the War intervened and prevented Bridgman from working on the theme; in any case, Bridgman was insufficiently versed in chemistry to recognise the need for metallic catalysts. After the War was over GE acquired high-pressure equipment

from Bridgman and did in-house research which eventually, in late 1954, when a method of reaching the very high temperatures and pressures required had been perfected and after the crucial role of catalysts had been established, led to the large-scale synthesis of industrial diamond grit at high temperatures and pressures. According to Hazen's book, roughly 100 tons of synthetic diamond (mostly grit for grinding and cutting tools) are now manufactured every year, "providing almost nine out of every ten carats used in the world". In recent years, methods have been perfected of making synthetic diamond in the form of thin sheets and coatings, by a vapour-based method operating at low pressure. This approach also has increasing applications, though they do not overlap with the pressure-based approach. This latest advance is an instance of *challenge and response*, rather like the great improvements made in crystalline transformer steel sheets to respond to the challenge posed by the advent of metallic glass ribbons.

The GE research program, although it was the most successful effort, was far from being the only attempt to make synthetic diamond. There was much research in Russia, beginning in the 1930s; language barriers and secrecy meant that this valuable work was not widely recognised for many years, until DeVries *et al.* (1996) published a detailed account. Another determined attempt to synthesise diamond which led to a success in 1953 but was not followed through was by the ASEA company in Sweden. This episode is racily told in Chapter 4 of Hazen's book under the title *Baltzar von Platen and the Incredible Diamond Machine*.

Hot isostatic pressing (HIP), a technique which was introduced in 1955 and became widespread in advanced materials processing from 1970 onwards, was developed by ASEA and derived directly from the Swedish diamond research in the early 1950s. In this apparatus, material is heated in a furnace which is held within a large (cold) pressure vessel filled with highly pressurised argon. Elaborate techniques, including reinforcement of the pressure vessel by pretensioned wire windings, had to be developed for this technique to work reliably. By HIP, microporosity within a material, whether caused during manufacture or during service, can be closed up completely. HIP has been used for such purposes as the containment of radioactive waste in ceramic cylinders, strength improvement of cemented carbides (Engel and Hübner 1978), the homogenisation of high-speed tool steels, the 'healing' of porous investment castings (by simply pressing the pores into extinction), and the 'rejuvenation' of used jet-engine blades again by getting rid of the porous damage brought about by creep in service. Lately, HIP has been widely used to permit complete densification of 'difficult' powder compacts. Apparently, HIP was even used at GE to repair damaged carborundum pressure-transmitting blocks needed for their production process. HIP is an excellent example of a process useful to materials engineers developed as spin-off from what was initially a piece of parepistemic research.

It appears that HIP was independently invented, also in 1955, at the Battelle Memorial Institute in Columbus, Ohio, under contract to the Atomic Energy Commission and with the immediate objective of bonding nuclear fuel elements with precise dimensional control.

The various densification mechanisms at different temperatures can be modelled and displayed in HIP diagrams, in which relative temperature is plotted against temperature normalised with respect to the melting-point (Arzt *et al.* 1983). This procedure relates closely to the deformation-mechanism maps discussed in Section 5.1.2.2.

Bridgman's personal researches, as detailed in his 1931 book, covered such themes as electrical resistivity, electrical and thermal conductivity, thermoelectricity and compressibility of solids, and viscosity of liquids. The ability to measure all these quantities in small pressure chambers is a mark of remarkable experimental skill. There is also a chapter on pressure-induced phase transformations, including what seem to have been the first studies of the pressure-induced polymorphs of ice (and 'heavy ice'). In recent decades research emphasis has shifted more and more towards polymorphism under pressure. Pressures now readily attainable in ordinary pressure chambers exceed 20 GPa, while minute diamond anvils have also been developed that permit X-ray diffraction under pressures well over 200 GPa. Nowadays, pressure effects are often created transiently, by means of shock waves, and studied by techniques such as X-ray flash radiography. Recent researches are reviewed by Ruoff (1991), and a lively popular account of these methods makes up the end of Hazen's (1999) book. A good example of a research programme that falls between several specialities (it is often classified as chemical physics) is the analysis of crystal structures of ice at different temperatures and pressures, pioneered by Bridgman in 1935. A few years ago, nine different ice polymorphs, all with known crystal structures, had been recorded (Savage 1988); by now, probably even more polymorphs are known. Indeed, many of the elements have been found to have pressure-induced polymorphs, which often form very sluggishly (Young 1991).

The impact of high pressures on crystal structure research generally is considerable, to the extent that the International Union of Crystallography has set up a high-pressure commission; a recent (1998) "workshop" organised by this commission at the Argonne National Laboratory in Illinois (home to a synchrotron radiation source) attracted 117 researchers. At the big Glasgow Congress of the International Union of Crystallography in 1999, the high-pressure commission held several meetings that attracted very varied contributions, summarised in IUCr (2000). One finding was that carbon dioxide forms a polymer under extreme pressure!

Robert Hazen's excellent 1999 book on the diamond-makers has been repeatedly cited. Earlier, he had brought out a popular account of high-pressure research

generally, under the title *The New Alchemists: Breaking Through the Barriers of High Pressure* (Hazen 1993).

The high-pressure community is now drawn from many fields of interest and many branches of expertise. A recent symposium report (Wentzcovich *et al.* 1998) gives a flavour of this extraordinary variety, drawing in not only earth science but microelectronics, supercritical phase transformations in fluids studied by chemical engineers (the wheel coming full circle), powder processing under extreme conditions, etc. One paper focuses on one characterisation tool, the Advanced Photon Source (a synchrotron radiation facility), which has been used in 11 different ways to characterise materials at 'ultrahigh pressures and temperatures', including time-resolved X-ray diffraction. Perhaps because the high-pressure parapisteme is so very diffuse, it has taken a long time for a journal exclusively devoted to the field to emerge: *High Pressure Research*. Much research on high pressures is still divided between materials-science and earth-science journals.

This summary shows how research undertaken by one brilliant scientist for his own interest has led to steadily enhanced experimental techniques, unexpected applications and a merging of many skills and interests.

4.2.4 Crystallography

In Chapter 3, from Section 3.1.1.1 onwards, I discuss a range of aspects of crystals – X-ray diffraction, polymorphism and phase transformations, crystal defects, crystal growth, polytypism, the relation of crystal structure to chemical reactivity, crystal chemistry and physics. All these topics belong, more or less closely, to the vast parapisteme of *crystallography*. In that Chapter, I treated the study of crystals as one of the central *precursors* of materials science, and so indeed it is, but all the above-mentioned component topics, and others too, were parts of a huge parapisteme because none of them was directly aimed, originally, at the solution of specific practical problems.

Crystallography is an exceptional parapisteme because of the size of its community and because it has an 'aristocracy' – the people who use X-ray diffraction to determine the structures of crystals. This probably came about because, alone among the parapistemes I have discussed, crystallographers have had their own scientific union, the International Union of Crystallography (IUCr), affiliated to the International Council of Scientific Unions (ICSU), since 1948. Its origin is discussed by a historian of ICSU (Greenaway 1996), who remarks that the IUCr "was brought into existence because of the development, not of crystallography, which had its origin in the 17th century, but of X-ray crystallography which originated in about 1913. By 1946 there were enough X-ray crystallographers in the world and in touch with each other for them to want to combine. Moreover,

though publication was important, a mere learned society would not quite meet their needs. *The reason for this was that their subject was already useful in throwing light on problems in other fields of science, pure and applied* (my italics). A Union, with its ICSU-guided links with other Unions, was a better form". We have seen in Chapter 3 that the old crystallographic journal, *Zeitschrift für Kristallographie*, was very tardy in recognising the importance of X-ray diffraction after 1912. The new Union, founded in 1948, created its own giant journal, *Acta Crystallographica*; as with some other journals founded in this period, the title resorts to Latin to symbolise the journal's international outlook. Incidentally, while the IUCr flourishes mightily, materials science and engineering has no scientific union. A social historian is needed to attempt an analysis of the reasons for this omission.

In addition to the overarching role of the IUCr, there are numerous national crystallographic associations in various countries, some of them under the umbrella of bodies like the Institute of Physics in Britain. I doubt whether there is any other *parepisteme* so generously provided with professional assemblies all over the world.

Metallurgists originally, and now materials scientists (as well as solid-state chemists) have used crystallographic methods, certainly, for the determination of the structures of intermetallic compounds, but also for such subsidiary *parepistemes* as the study of the orientation relationships involved in phase transformations, and the study of preferred orientations, alias 'texture' (statistically preferential alignment of the crystal axes of the individual grains in a polycrystalline assembly); however, those who pursue such concerns are not members of the aristocracy! The study of texture both by X-ray diffraction and by computer simulation has become a huge sub-subsidiary field, very recently marked by the publication of a major book (Kocks *et al.* 1998).

Physics also is intimately linked with crystallography in many ways. One mode of connection is through the detailed study of crystal perfection, which substantially influences the diffraction behaviour: the most recent review of this involved topic, which has been studied since the earliest days of X-ray diffraction, is by Lal (1998) (his paper is titled 'Real structure of real crystals'). A famous systematic presentation of the mathematical theory of crystal anisotropy, still much cited, is a book by Nye (1957); this study goes back in its approach to the great German mineralogists of the 19th century. Nevertheless, physicists feel increasingly uneasy about the proper nature of their linkage with crystallography; thus in 1999, the Physical Crystallography Group of the (British) Institute of Physics decided to change its name to 'Structural Condensed Matter Physics Group'; the word 'crystallography' has vanished from the name.

Perhaps the last general overview of crystallography in all its many aspects, including crystal chemistry and crystal physics and the history of crystallographic concepts, as well as the basics of crystal structure determination, was a famous book

by the Braggs, father and son (Bragg and Bragg 1939), both of them famous physicists as well as being the progenitors of X-ray diffraction.

Chemical crystallographers are also beginning to reconsider their tasks. Thus, in a prologue to a new book (Rogers and Zaworotko 1999), G.R. Desiraju comments: "...the determination of most small-molecule structures became a straightforward operation and crystallographic databases began to be established..." (see Section 13.2.2). The interest of the chemical crystallographer, now more properly called a structural chemist, has changed from crystal structure determination to crystal structure synthesis. The question now becomes 'How does one go about designing a particular crystal structure that is associated with a particular architecture, geometry, form or function?'.

The broad appeal of crystallography across a wide gamut of sciences is demonstrated by a book brought out to mark the 50th anniversary of *Acta Crystallographica* and the International Union of Crystallography (Schenk 1998). Physics, chemistry, biochemistry, superconductivity, neutron diffraction and the teaching of crystallography all find their champions here; several of these essays are written with a historical emphasis.

The 'aristocrats' who determine crystal structures have garnered a remarkable number of Nobel Prizes; no fewer than 26 have gone to scientists best described as crystallographers, some of them in physics, some in chemistry, latterly some in biochemistry. Crystallography is one of those fields where physics and chemistry have become intimately commingled. It has also evinced more than its fair share of quarrelsomeness, since many physicists regard it as a mere technique rather than a respectable science, while crystal structure analysts, as we have seen, were for years inclined to regard anyone who studied the many other aspects of crystals as second-class citizens.

It is striking that, in spite of the huge importance of crystallography in physics, chemistry, biochemistry, pharmacology and materials science, few degree courses leading to bachelor's degrees in crystallography are on record. The famous Institute of Crystallography in Moscow in its heyday gave degrees in crystallography (it certainly trained students at the research level), as did some other Russian institutes; Birkbeck College in London University has a famous Department of Crystallography, based on the early fame of J.D. Bernal, which awards degrees, and there is a degree course in crystallography in the Netherlands. There was a brief attempt to award a degree in crystallography in the physics department of Cambridge University, but it did not last. Now students in Cambridge who wish to specialise early in this *parepisteme* need to take a degree in earth sciences. So, the small *parepisteme* of colloid science and the large *parepisteme* of crystallography are in this respect on a par – one cannot easily get degrees in colloid science or in crystallography.

4.2.5 Superplasticity

To conclude this selection of examples from the wide range of *parepistemes* in MSE, I have chosen a highly specialised one which has developed into a major industrial technique. Superplasticity has recently been defined, in a formulation agreed at a major international conference devoted to the subject, as follows: “Superplasticity is the ability of a polycrystalline material to exhibit, in a generally isotropic manner, very high tensile elongations prior to failure”. In this connection, ‘high’ means thousands of percent; the world record is currently held by a Japanese, Higashi, at 8000% elongation.

The first recorded description of the phenomenon was in 1912 by an English metallurgist (Bengough 1912). He studied a two-phase brass, pulling it at a modest strain rate at a range of temperatures up to 800°C, and securing a maximum strain of $\approx 160\%$ at 700°C. His thumbnail description is still very apposite: “A certain special brass... pulled out to a fine point, just like glass would do, having an enormous elongation”. In the following 35 years occasional studies of various two-phase alloys confirmed this type of behaviour, which mimics the behaviour of glasses like pyrex and amorphous silica while the alloys remain crystalline throughout. Thus, Pearson (1934) stretched a Bi–Sn alloy to nearly 2000% (see Figure 4.6). The stress σ required to maintain a strain rate $d\varepsilon/dt$ is approximately given by $\sigma = (d\varepsilon/dt)^m$; for a glass, $m = 1$, for metals it is usually much lower. When m is high, the formation of a neck in tension is impeded because in a neck, the local strain rate becomes enhanced and

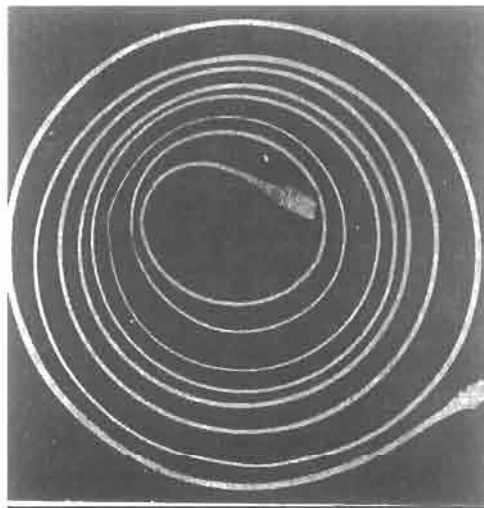


Figure 4.6. Pearson’s famous photograph in 1934 of a Bi–Sn alloy that has undergone 1950% elongation.