1 Spectacular Advances

Figure 1.1: Modern electron microscope with an accelerating voltage of one million volts. (Photo: A. Tonomura).

Electrons in Action: Roads to Modern Computers and Electronics. Rudolf Huebener Copyright © 2005 Wiley-VCH Verlag & Co. KGaA ISBN: 3-527-40443-0

During the second half of the last century the physics of solids has experienced tremendous growth, for which many important basic steps had already been prepared during the first half of the century. An early decisive impulse for these developments came from the discovery of X-rays in 1895 in Würzburg, Germany, by W. C. Röntgen. Soon afterwards, this discovery led to the first observation of X-ray diffraction in crystals by M. von Laue in 1912 in Munich. W. H. Bragg, Professor in Leeds, England, together with his son W. L. Bragg at the early age of only 22 years, then started the systematic analysis of crystal structures by means of X-ray diffraction.

Today, research dealing with the physics of solids has an impressively wide scope, if for no other reason than the fact that solids are always needed to fabricate useful or nice things, in contrast to the totally different role of liquids and gases. The exact knowledge of the physical properties of materials that we use today becomes more and more important the further we advance in the field of high technology. The large effort of research and development within the area of solid state physics becomes obvious if one looks at the program books for the relevant annual meetings of, say, the German Physical Society (DPG) or the American Physical Society (APS) which these days contain up to more than 2000 pages.

Often, the technological applications provide the key motivation for strong basic research in solid state physics. We illustrate this by the following two examples. On January 10, 1954, an English passenger airplane of the Comet type broke apart at 8200 m altitude in the Mediterranean near the isle of Elba without any prior warning and crashed into the sea. With only 3681 flight hours, the plane was relatively new. The search for the cause of the accident turned out to be extremely difficult, even though people worked feverishly to clarify the cause of the terrible crash. Since the cause of the accident continued to remain unknown it was finally concluded that the crash must have been the result of an unfortunate combination of several bad effects. Hence, on March 23, 1954, the grounding order for all airplanes of the same type, immediately issued on the day of the accident, was lifted again. Prior to this, a total of 62 modifications had been introduced in all Comet airplanes in operation or under construction. In this way it was hoped to exclude any possible cause of the accident (Figure 1.2). Then a completely unexpected dramatic event happened. On April 8, i. e., only 16 days following the resumption of the regular flight operation, another

Comet airplane with only 2704 hours of flight operation crashed into the Mediterranean near Naples. Again, at a high altitude of 10 000 m this time, the plane suddenly apparently broke apart. Now the situation became extremely serious. The causes had to be found at the highest level, and all available means had to be utilized. After analysis of the many different possibilities, problems related to what is now called material fatigue, in particular associated with the wings, came to the center of attention. As a consequence, the complete fuselage of an airplane was dumped into a huge tank filled with water in order to expose it to changing, and in particular to cyclical, mechanical loads. In this way, it was found that, after some time, fatigue effects appeared on the wings. However, the fatigue problems on the fuselage itself were much more severe. Finally, the evidence became clear that the mechanical load during testing caused cracks in the fuselage, and that all the cracks originated at the rectangular corners of the cabin windows. The causes of both plane crashes had been found. However, this event also put to an abrupt end the British leading role in air traffic.

Because of these dramatic developments, intensive research activities were begun at the same time in many places. Until then only little was known about the phenomenon of material fatigue, its effect on the mechanical properties of materials, and the mechanisms leading to the development of microcracks.

In this context of the material fatigue experienced fifty years ago with the Comet passenger airplane, it is interesting to note that the current development of the largest passenger airplane, which has ever been constructed, the Airbus A 380, includes an extensive and careful mechanical material fatigue testing procedure by means of hydraulic systems, as a critical step. Starting in 2005 the complete A 380 airplane, consisting of the whole fuselage and the wings, will be exposed for 26 months to mechanical loads varying with time and simulating a total number of 47 500 flight cycles. This testing load program corresponds to the 25 year lifetime of the A 380 airplane.

As a second example, we recall the possible difficulties expected more than 50 years ago during the operation of the inner components of the first nuclear reactors. At that time hardly anything was known about the behavior of, say, graphite, when it is utilized for slowing down the neutrons which are emitted during nuclear fission within the reactor. Would it be possible that during their irradiation with the highly energetic neutrons, the carbon atoms of the graphite lattice could be

Figure 1.2: Comet jet-aircraft beginning a test flight after the crash of a plane in the Mediterranean near the isle of Elba. (Photo: ullstein bild).

ejected out of their regular lattice sites, eventually leading to an energetically highly excited material, releasing abruptly its stored excess energy in an explosion like dynamite? Such problems concerned the scientists involved in the early reactor experiments. The American scientist E. P. Wigner, originally from Hungary (later a Nobel laureate and famous for his theoretical work on mathematical group theory and symmetry principles and their role in atomic, nuclear, and elementary particle physics) was one of the first who theoretically analyzed the physical properties of lattice defects and radiation damage in crystals. At that time, a young co-worker of Wigner, F. Seitz, performed the first theoretical calculations on this subject (Figure 1.3). Both scientists introduced the concept of the "Wigner–Seitz cell" into solid state physics. Following these initial steps, the field of structural lattice defects in crystals has developed into an important subfield of solid state physics, being investigated today in many laboratories. In 1940 F. Seitz also published the first general textbook on solid state physics: "The Modern Theory of Solids".

An enormously important development took place with respect to microelectronics. Here the physics of solids has resulted in a total paradigm change in electronic technology. It was M. Kelly, one of the top-level managers of the famous American Bell Laboratories in Murray Hill in the Federal State of New Jersey, who realized at the end of the Second World War that the old mechanical relays and the evacuated amplifying tube made from glass had to be replaced by something

Figure 1.3: Eugene P. Wigner (left photo: Deutsches Museum) and Frederick Seitz (right: private photo).

better. To Kelly, a highly promising candidate appeared to be the crystal, if it had suitable electrical conduction properties. Therefore, at the Bell Laboratories a special group of scientists was organized, which was supposed to explore the electrical conduction properties of solids. At the center of everyone's attention then stood the semiconductor crystals of germanium and silicon. Already, relatively soon afterwards, an extremely momentous event had been the invention of the transistor by J. Bardeen, W. H. Brattain, and W. Shockley. On December 23, 1947, they demonstrated the transistor for the first time to the directors of their company. Subsequently, as a new electronic device, the transistor, underwent intensive further development and improvement. Without a doubt, this invention represented the start of the modern age of digital electronics.

These big advances in the field of solid state physics, of course, were accompanied by similar advances in instrumental techniques and methods. Here we must mention the exploration of the regime of very low temperatures. In 1908 the Dutch scientist H. Kamerlingh Onnes in Leiden achieved for the first time the liquefication of the noble gas helium. With this success the low-temperature range down to 4 Kelvin

(minus 269 ◦Celsius) became accessible. In this context the most spectacular event was the subsequent discovery of superconductivity by Kamerlingh Onnes in 1911. Until the thirties, the number of laboratories equipped to perform experiments with liquid helium worldwide could be counted on the fingers of one hand. In contrast, today about 800 helium liquefiers are operating worldwide (Figure 1.4).

Figure 1.4: Modern plant for liquefying the noble gas helium. On the right one can see the liquefier; on the left, the storage tank; and in front of it, a transport vessel for liquid helium. (Photo: Linde).

Eventually, the available experimental regime was extended to lower and lower temperatures. In particular, we mention a technique relying on the elementary atomic magnets of a paramagnetic substance. This technique consists of the following sequence of steps. Initially, a paramagnetic salt pill is precooled to about 1 Kelvin, in order to reduce considerably its content of thermal energy. Subsequently, the elementary magnets in the salt pill are all oriented in one direction by a strong magnetic field, and simultaneously the heat of magnetization is removed, being deposited in the environment. In the next step, the salt pill is thermally decoupled from its environment. Then the magnetic field is turned off.

Now the pill is thermally isolated, and the directional disorder of the elementary magnets gradually reappears. As a necessary consequence, the temperature of the salt pill drops at the same time. In this way low temperatures of only a few thousandth Kelvin can be reached. This method of "adiabatic demagnetization" was proposed in 1926 by the Dutch scientist P. Debye and in 1927 by the American W. F. Giauque. In 1933 the method was demonstrated experimentally for the first time. The extended application of this principle to the elementary magnets of atomic nuclei had already been proposed in 1934 by the Dutch scientist C. J. Gorter and in 1935 by N. Kurti and F. E. Simon from Oxford. The cooling effect due to this nuclear demagnetization was experimentally realized for the first time in 1956. Using this technique, extremely low temperatures down to one millionth Kelvin or lower could be reached. However, at such low temperatures it becomes more and more difficult to establish thermal equilibrium between the different components of the solid, namely the electrons and their elementary magnets, the lattice vibrations, and the elementary magnets of the atomic nuclei.

Because of their Jewish origin, Kurti and Simon had to leave Germany in 1933 when Hitler took over the government. Earlier, both had worked first in Berlin and then at the Technical University in Breslau (today Wroclaw) and the English scientist F. A. Lindemann (later Viscount Cherwell) had arranged for a position for both of them at the Clarendon Laboratory in Oxford, England. As director of the Clarendon Laboratory Lindemann had done exactly the same at the time also for the two brothers Fritz and Heinz London, and for K. Mendelssohn. After they had left Germany, during subsequent years, all these people distinguished themselves by outstanding contributions to physics at low temperatures.

An apparatus often used today for reaching temperatures much below 1 Kelvin is the mixing cryostat (Figure 1.5). In this cryostat the two isotopes of the noble gas helium, which differ only by the number of neutrons in their atomic nuclei $({}^{3}$ He with a single neutron and ⁴He with two neutrons), are pumped through several stages of heat exchangers, such that within the mixing chamber located at the coldest end of the instrument an almost pure liquid ³He phase is collected directly above a liquid mixed phase of 3 He and 4 He. For this technique to operate, the starting temperature must already have been lowered to 1 Kelvin by precooling. During operation, 3 He atoms from the upper concentrated phase are dissolved continuously in the lower, much more

diluted, phase. In many ways this scheme resembles a regular evaporation process, in which the upper phase corresponds to the liquid and the lower phase to the vapor. As a final result, a continuous cooling of liquid helium is achieved.

Figure 1.5: Mixing cryostat for cooling down to temperatures well below 1 Kelvin. The coldest end with the mixing chamber is located at the bottom. On the top one can see the flange for mounting into the cryogenic container, which can also be evacuated. (Photo: Oxford).

With this apparatus the attached sample to be studied can also be cooled continuously. The lowest temperatures which can be reached are a few thousandth Kelvin. The principle of the mixing cryostat was proposed for the first time in 1951 by Heinz London. The first prototype was operated in 1965. Together with his brother Fritz London, Heinz London also had proposed an early theory of superconductivity.

In addition to the continuing improvements in experimental instruments and to the refinements of measuring techniques, sample preparation and the development of materials also saw much progress. Here an important step was the production of single crystals with extremely high purity. It was such ultra-pure single crystals which allowed the

Figure 1.6: Silicon single crystal. (Photo: Wacker-Chemie Inc.).

exact determination of many physical properties of materials and the achievement of a theoretical understanding based on these data (Figure 1.6). The growing of large single crystals starts by dipping a little seed crystal under an inert gas atmosphere into the melt of the same material and then pulling it out again at a slow and well regulated speed. In this way, during solidification of the melt, the exact atomic order of the seed crystal will be reproduced. Record sizes of such cylindrical single crystals up to more than one meter in height and nearly half a meter in diameter have been achieved. The concentration of atomic impurities in such a crystal can be reduced further by means of the "zone melting process". During this process the total cross-section of a short length of the crystal is heated up to the melting temperature by means

of, say, eddy current heating, while this heating zone is slowly moved from one end of the crystal to the other. In the resulting temperature gradient the atomic impurities are carried along to one end of the crystal. If necessary, this process can be repeated several times. The impurity concentration of silicon single crystals, routinely achieved today in the semiconductor industry, amounts to only about a single impurity atom within one billion silicon atoms.

Figure 1.7: Egg-shaped research reactor ("Atomei") in Garching near Munich. In the building on the left the new research reactor is located, which has only recently been completed. (Photo: Albert Scharger).

The spectacular advances in our physical understanding of the microscopic properties of solids was closely coupled to the progress of the instruments and methods available for the analysis of materials. In addition to the investigation of the structure of crystals by means of X-ray diffraction already mentioned, starting in the 1950s the diffraction of neutrons was also utilized more and more for clarifying crystal structures. For this purpose, special nuclear reactors built only for research purposes served as neutron sources. As an example we mention the egg-shaped research reactor ("Atomei") built in the sixties at the Technical University of Munich in Garching, Germany (Figure 1.7). In some sense as a training ground, this reactor then turned out to become the point of origin for the much larger research reactor of the German–French, Laue–Langevin Institute in Grenoble. Similar con-

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struction projects for research reactors also existed in other countries with a highly developed industry.

In the same way as often happens with new ideas, the invention of the electron microscope initially had to withstand great difficulties and rejection. It all began with two Ph. D. students, namely E. Ruska and B. von Borries, who had joined the group of M. Knoll at the Chair of High-Voltage Engineering and Electric Plants (occupied by A. Matthias) at the Technical University of Berlin during December 1928 and April 1929, respectively. Here, at first both worked on the improvement of the cathode ray oscilloscope. Because of the experience gained, before long they had developed the idea that beams of fast electrons can be used for generating a magnified image in a new type of microscope. On March 17, 1932, E. Ruska and B. von Borries submitted their first and basic patents on the future electron microscope. However, a few large hurdles still remained to be overcome. "Why do we need electron microscopes, since we have light microscopes?" was the question that people were asking. However, soon both young scientists had a breakthrough. The Company Siemens & Halske in Berlin agreed to pick up the idea and prepared employment contracts for B. von Borries and E. Ruska. On December 7, 1937, the first electron microscope built by Siemens was demonstrated to the Company directors (Figure 1.8).

After only three years of development, in terms of its spatial resolution the electron microscope had outpaced the light microscope. Starting in 1939, an initial series of the Supermicroscope ("Übermikroskop"), as it was called at the time, was offered for sale by Siemens.

Again, the underlying basic concept of this microscope is the quantum-mechanical wave character of elementary particles, which had been proposed for the first time by the Frenchman L. V. de Broglie in his dissertation in 1924. The direct experimental proof of the wave nature of the electrons was provided subsequently in 1927 by the two Americans C. J. Davisson and L. H. Germer of the Bell Telephone Laboratories who showed that electrons are diffracted by the atomic lattice of crystals. During imaging based on the diffraction of waves, the spatial resolution is always limited by the wavelength. The shorter the wavelength, the correspondingly smaller are the structures that can be spatially resolved. The wavelength of the beam electrons is inversely proportional to the square-root of the accelerating voltage. At an electric voltage of 10 000 volts we have a wavelength of $\lambda = 1.2 \times 10^{-2}$ nm

Figure 1.8: An early electron microscope from Siemens. (Photo: TU Berlin).

(nanometer, shortened nm, corresponds to one millionth mm). On the other hand, the wavelength of visible light is much larger, $\lambda = 400-$ 800 nm, and the achieved spatial resolution is correspondingly much weaker.

Already in the 1950s, electron microscopy had celebrated a big success, along with many other successes, by imaging the structural defects in the crystal lattice, as discussed above, and by clarifying the phenomenon of material fatigue. In the latter case the "crystal dislocations" play a central role. They were observed directly for the first time in 1956 at the Batelle Institute in Geneva in stainless steel and at the Cavendish Laboratory in Cambridge in aluminum. Eventually, electron microscopes were built for ever increasing accelerating voltages. Today we have instruments with an accelerating voltage of one million volts (Figure 1.1).

For the analysis of materials, beams of fast electrons have also been utilized in another important instrument: the scanning electron micro-

scope. For this, pioneering research was done again in the thirties by M. Knoll at the Technical University in Berlin, mentioned before, and by M. von Ardenne in his Laboratory in Berlin-Lichterfelde. An electron beam collimated down to an extremely small diameter of only 1–10 nm is scanned over the surface of the object to be investigated. Simultaneously, a suitable signal induced by the electron beam in the sample is recorded as a function of the spatial beam coordinates on the sample surface within the scanning window. Correct electronic signal processing then yields a two-dimensional image of the object. To generate the response signal one can use several effects. For example, the emission of secondary electrons due to the beam irradiation is quite often used. However, the beam-induced local change of a sample property such as the electrical resistivity can also provide the signal for the image. Today, the signal based on the change in electrical resistivity is often utilized for imaging structures in thin layers of semiconductors or superconductors. In the case of superconductors, spatially resolved images relating to their superconductivity can be obtained if the sample is cooled to sufficiently low temperatures during scanning with the electron beam.

Recently, the scanning principle for imaging was extended also to light beams. However, a necessary prerequisite for this was the availability of laser beams with their extremely narrow collimation. Today, laser scanning microscopes are widely used in many fields.

An important milestone during the advances of methods for the analysis of materials has been the construction of the first scanning tunneling microscope by G. Binnig and H. Rohrer of the IBM Research Laboratory in Rüschlikon near Zürich, Switzerland. Their first patent application dealing with the scanning tunneling microscope was submitted in January 1979. In their instrument the surface to be investigated is mechanically scanned with a tiny metal tip. Using piezoelectric actuators, the metal tip can be moved in three dimensions with extremely high sensitivity. During the scanning process the sample surface is approached by the tip as closely as about 1 nm. Simultaneously, the quantummechanical electric tunneling current is measured running between the tip and the sample surface, if an electric voltage is applied, even though a metallic contact between both does not exist. (The explanation of the effect of quantum mechanical tunneling had been one of the early major successes of the new theory of quantum mechanics). Because of the strong exponential dependence of the tunneling current on the distance

between the tip and the sample surface, one can achieve that the tunneling current is limited only by a few or even the last single atom sticking out of the tip. In this way, today one routinely obtains atomic resolution in the lateral direction with this technique (Figure 1.9). Very recently, even subatomic structures of silicon atoms due to the different electron orbitals, have been observed in the images (Figure 1.10).

Figure 1.9: Scanning tunneling microscope. The instrument is mounted on a flange for operation in ultra-high vacuum. (Photo: OMICRON Nano Technology).

Soon after the invention of the scanning tunneling microscope, the mechanical scanning principle was extended to several other types of interaction between the probing tip and the sample surface. In particular, we mention the atomic force and the magnetic force microscopes. In the first case, the mechanical force between the probing tip and the sample surface is utilized. The second case is based on a magnetic tip probing the magnetic sample properties. In recent years special research effort has been concentrated on the extension of the techniques we have discussed to very low temperatures and to the presence of high magnetic fields.

Finally, we emphasize that most of the techniques for material analysis discussed above are restricted to the sample surface and its immediate neighborhood (Figure 1.11).

Figure 1.10: Image of the individual atoms of a section of 5 nm \times 5 nm area on the surface of a silicon crystal, generated by means of atomic force microscopy. On the silicon atoms we can see a subatomic structure resulting from the electron orbitals. (Photo: F. J. Giessibl).

In many cases the developments we have outlined were accompanied by the award of the Nobel Prize for Physics and in some cases for Chemistry to the people involved. In order to illustrate this, in the Appendix we have listed all Nobel Laureates who have a close relationship with the physics of solids.

Figure 1.11: The picture shows a ring of iron atoms placed on a copper surface. In this way an artificial coral reef consisting of 48 iron atoms has been created on an atomic scale. The circular lines appearing within the ring are due to the density of the electrons existing within the ring. (Photo: Almaden Research Center (2000)).