One-Dimensional Metals

Siegmar Roth

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Physics and Materials Science

VCH Weinheim • New York • Basel • Cambridge • Tokyo

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Published jointly by
VCH Verlagsgesellschaft mbH, Weinheim (Federal Republic of Germany)
VCH Publishers, Inc., New York, NY (USA)

Editorial Directors: Dr. Peter Gregory, Dr. Ute Anton
Production Manager: Dipl.-Ing. (FH) Hans Jörg Maier

Library of Congress Card No. applied for.

A catalogue record for this book is available from the British Library.

Deutsche Bibliothek Cataloguing-in-Publication Data:
Roth, Siegmar:
One-dimensional metals : physics and materials science /
Siegmar Roth. - Weinheim ; New York ; Basel ; Cambridge ; Tokyo : VCH, 1995
ISBN 3-527-26875-8

Printing: betz-druck gmbh, D-64291 Darmstadt. Bookbinding: Wilhelm Osswald & Co, D-67433 Neustadt
Cover design: Graphik & Text Studio Zettlmeier-Kammerer, D-93164 Laaber-Waldetzenberg.
Printed in the Federal Republic of Germany.

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Advanced Materials
The leading journal in high-tech materials science
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ISSN 0935-9648

Distribution
VCH, P. O. Box 10 11 61, D-69451 Weinheim (Federal Republic of Germany)
Switzerland: VCH, P. O. Box, CH-4020 Basel (Switzerland)
United Kingdom and Ireland: VCH (UK) Ltd., 8 Wellington Court, Cambridge CB1 1HZ (England)
USA and Canada: VCH, 220 East 23rd Street, New York, NY 10010-4606 (USA)
Japan: VCH, Eikow Building, 10–9 Hongo 1-chome, Bunkyo-ku, Tokyo 113 (Japan)

ISBN 3-527-26875-8

Preface and Acknowledgments

This book originated from lectures on "Physics in One-Dimension" given at the University of Karlsruhe in the 1980s. I am grateful to all the students who contributed by asking questions. Some of them, later on, became Ph.D. students at my research group in Stuttgart.

Style and content of the book reflect the everyday research work of a interdisciplinary and international research group where people of different background have to quickly catch-up on basic concepts in order to meet on equal terms for discussions.

The reader is expected to have some basic knowledge of science or engineering, for example, of physics, chemistry, biology, or materials science. To consolidate this knowledge he/she will have to consult textbooks on experimental physics, as well as on organic, inorganic, and physical chemistry. But the present book should help to forge links, and with these links the monographs recommended in the Appendix should be accessible. It should also be possible to follow international topical meetings. I hope that some of the aspects of the book are so interesting that they are even attractive to complete neophytes or to outsiders, and that some features will also appeal to the experienced researcher.

My thanks are due to all members of our team (Lidia Akselrod, Tarik Abou-Elazab, Teresa Anderson, Marko Burghard, Hugh Byrne, Claudius Fischer, Thomas Rabenau, Michael Schmelzer, Manfred Schmid, Andrea Stark-Hauser, Andreas Werner). Without permanent discussions in the lab's coffee corner the book would not have been possible. Particular thanks to Andrea Stark-Hauser, who not only did all the typing but was also engaged in collecting references and figures. Manfred Schmid assisted in the preparation of technical drawings and the cartoons were drawn by Günter Wilk. Teresa Anderson, Hugh Byrne and Andreas Werner went through my first drafts and generated major inputs to the final phrasing of the text which was ultimately polished by the experts of VCH Verlag and with whom it was a pleasure to co-operate.

The whole team benefited from the cooperation within the Sonderforschungsbereich "Molekulare Elektronik — physikalische und chemische Grundlagen" of the Deutsche Forschungsgemeinschaft, within the European BRITE/EURAM Project HICOPOL (comprising the groups in Stuttgart, Karlsruhe, Montpellier, Nantes, Strasbourg, and Graz) and within the European ESPRIT Network NEOME (Austria, Belgium, Denmark, England, France, Germany, Italy, Netherlands, Sweden, Switzerland).

Siegmar Roth April 1995

Biography

After studying physics at the University of Vienna, Siegmar Roth carried out his thesis work at the reactor center in Seibersdorf, Austria, and received his Ph.D. at the institute of Professor Erich Schmid. From 1968 – 1970 he worked at the Siemes Research Laboratories in Erlangen, Germany, on the solid-state physics of novel semiconductors. After a three-year stay at the High Flux Reactor of the Institute Laue Langevin and four years at the High-Field Magnet Laboratory, both in Grenoble, France, where his research centered on superconductors, he joined the Max-Planck-Institut für Festkörperforschung in Stuttgart, Germany. He is currently head of the Conductive Polymer Group.

Contents

1 Introduction

1.1 Dimensionality

Dimensionality is an intellectually very appealing concept and speaking of a dimensionality other than three will surely attract some attention. Some years ago it was fashionable to admire physicists who apparently could "think in four dimensions" in striking contrast to Marcuse's "One-Dimensional Man" [1]. Physicists

Figure 1–1: Simultaneously with Herbert Marcuse's book "One-Dimensional Man" [1], which widely influenced the youth movement of the 1960s, W.A. Little's paper on "Possibility of Synthesizing an Organic Superconductor" [2] was published, motivating many physicists and chemists to investigate low-dimensional solids.

would then respond with the understatement: "We only think in two dimensions, one of which is always time. The other dimension is the quantity we are interested in, which changes with time. After all, we have to publish our results as two-dimensional figures in journals. Why should we think of something we cannot publish?" (Figure 1–1).

This fictitious dialogue implies more than just sophisticated plays on words. If physics is what physicists do, then in most parts of physics there is a profound difference between the dimension of time and other dimensions, and there is also a logical basis for this difference [3]. In general, the quantity which changes with time and which "physicists are interested in" is one property of an object. The object in question is imbedded in space, usually in the three-dimensional space of our common-day experience. In addition, the object commonly has a certain length, width and thickness and is therefore also three-dimensional. Objects may be very flat such as flounders, saucers or oil films with greater length and width than thickness. In this case thickness can be negligibly small. Such objects can be regarded as (approximately) two-dimensional. Similarly, eels and wires are (nearly) one-dimensional. In another example, the motion of an object is restricted to two dimensions like that of a boat on the surface of the sea (hopefully) or to one dimension like that of a train on its track (again hopefully). According to our everyday experience one- and two-dimensional objects and one- and two-dimensional motions actually seem more common than their three-dimensional counterparts, so low-dimensionality should not be spectacular. Perhaps that is the reason for the introduction of non-integer ("fractal") dimensions [4]. Not much imagination is necessary to assign a dimensionality between one and two to a network of roads and streets — more than a highway and less than a plane. It is a well-known peculiarity that, for example, the coastline of Scotland has the fractal dimension of 1.33 and the stars in the universe that of 1.23.

Solid-state physics treat solids both as objects and as the space in which objects of physics exist: e. g., various silicon single crystals can be compared with each other, or they can be considered as the space in which electrons or phonons move. On one hand the layers of a crystal, for instance, the *ab*-planes of graphite, can be regarded as two-dimensional objects with certain interactions in-between them that can be discussed. On the other hand they are the two-dimensional space in which electrons move rather freely. Similar considerations apply to the (quasi) one-dimensional hydrocarbon chains of conducting polymers.

1.2 Approaching One-Dimensionality from Outside and from Inside

There are two approaches to low-dimensional or quasi low-dimensional systems in solid-state physics: geometrical shaping as an "external" and increase of anisotropy as an "internal" approach. For the external approach, let us take a wire and draw it until it gets sufficiently thin to be one-dimensional (Figure 1–2). How thin will it have to be? Certainly thin compared to a microscopic parameter, as for example, the average free path of an electron or the Fermi wavelength.

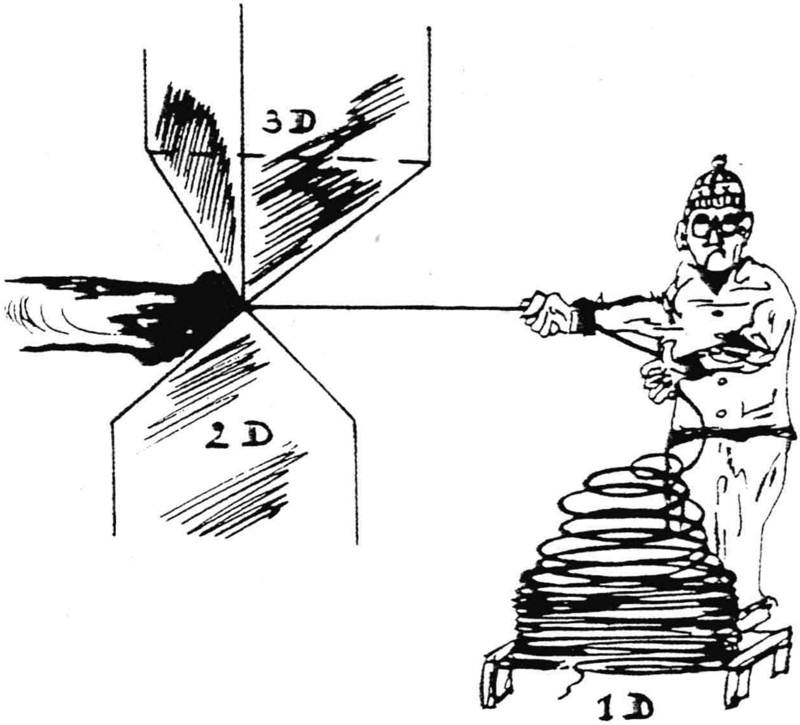

Figure 1–2: An "external approach" to one-dimensionality. A man tries to draw a wire until it is thin enough to be regarded as one-dimensional. Metallic wires can be made as thin as 1 μm in diameter, but his is still far away from being one-dimensional. (By lithographic processes semiconductor structures can be made narrow enough to exhibit one-dimensional properties.)

It will largely depend on the chosen measurement system which of the microscopic parameters is the decisive one. Does the wire have to be drawn so extensively to finally become a monatomic chain?

The Fermi wavelength becomes relevant when discussing the eigenstates of the electrons (we will learn more about the Fermi wavelength in Chapter 3). If electrons are confined in a box, quantum mechanics tells us that the electrons can have only discrete values of kinetic energy. The energetic spacing of the eigenvalues depends on the dimensions of the box, the smaller the box the larger the spacing (Figure 1–3):

$$\Delta E_L = h^2/2m\ (\pi/L)^2 \tag{1.1}$$

where ΔE_L is the spacing and L is the length of the box. The Fermi level is the highest occupied state (at absolute zero). The wavelength of the electrons at the

Fermi level is called the Fermi wavelength. If the size of the box is just the Fermi wavelength, only the first eigenstate is occupied. If the energy difference to the next level is much larger than the thermal energy ($\Delta E_L >> kT$), there are only completely occupied and completely empty levels and the system is an insulator. A thin wire is a small box for electronic motion perpendicular to the wire axis, but it is a very large box for motions along the wire. Hence in two dimensions (radially) it represents an insulator, in one dimension (axially) it is a metal!

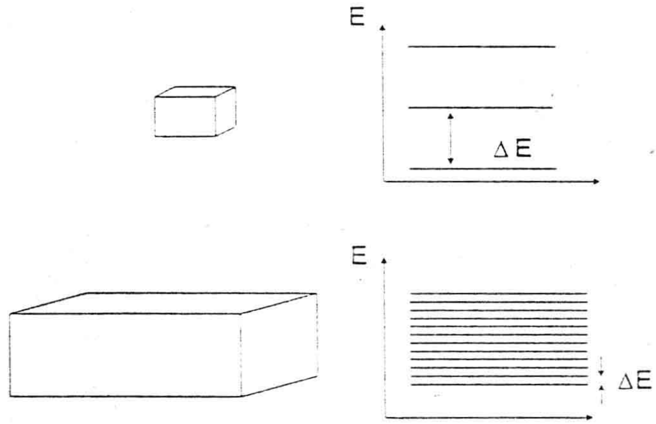

Figure 1–3: Electrons in small and large boxes and energy spacing of the eigenstates.

If there are only very few electrons, the Fermi energy is small and the Fermi wavelength fairly large. This is the case for semiconductors at very low doping concentrations. Wires of such semiconductors are already one-dimensional if their diameter is of the order of some 100 Ångstroms.

Such thin wires can be fabricated from silicon or from gallium arsenide by lithographic techniques and effects typical for one-dimensional electronic systems have been observed experimentally [5]. Systems with high electron concentrations have to be considerably thinner if they are to be one-dimensional. It turns out that for a concentration of one conducting electron per atom we really need a monatomic chain!

Experiments on single monatomic chains are very difficult, if not impossible, to perform. Therefore, typically a bundle of chains rather than one individual chain is used. An example for such a bundle is the polyacetylene fiber, consisting of some thousand polymer chains, closely packed with a typical interchain distance of 3 to 4 Ångstroms. Certainly there will be some interaction between the chains; however, in case of small interchain coupling, it can be assumed that just the net sum of the individual chains determines the outcome of the experiment (Figure 1–4).

Another method of geometrical shaping employs surfaces or interfaces (Figure 1–5). The surface of a silicon single crystal is an excellent two-dimensional system and there are various ways of confining charge carriers to a layer near the surface. Actually, the physics of two-dimensional electron gases are an important

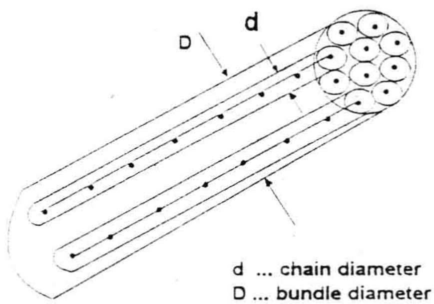

Figure 1–4: Experiments on individual chains are difficult to perform. But bundles of chains are quite common, for example, fibers of polyacetylene.

part of today's semiconductor physics [6] and most of the two-dimensional electron systems are confinements to surfaces or interfaces. The most fashionable effect in a two-dimensional electron gas is the quantized Hall effect or von Klitzing effect [7]. A one-dimensional surface, i.e., the edge of a crystal, is much more difficult to prepare and hardly of any practical use. If one argues, however, that exposing a sample to a magnetic field reduces the effective dimensionality by one, then a silicon surface in a magnetic field would be an excellent example of a one-dimensional electronic system. In fact, reducing von Klitzing's sample to "edge channels" is one way of explaining the von Klitzing effect [8].

The "internal approach" to one-dimensional solids comprises the gradual increase of anisotropy. In crystalline solids the electrical conductivity is usually different in different crystallographic directions. If the anisotropy of the conductivity is increased in such a way that the conductivity becomes very large in one direction and almost zero in the two perpendicular directions, a nearly one-dimensional conductor will result. Of course, there is no simple physical way to increase the anisotropy. However it is possible to look for sufficient anisotropy in already existing solids which could be regarded as (quasi) one-dimensional. Some anisotropic solids are compiled in the next chapter of this book. How large should the anisotropy be to meet one-dimensionality? A possible answer is: "Large enough to lead to an open Fermi surface".

The Fermi surface is a surface of constant energy in "reciprocal space" or momentum space (Fermi surface and reciprocal space will be discussed in Chapter 3 in greater detail). For an isotropic solid, the Fermi surface is spherical.

If the electrical conductivity is large in one crystallographic direction and small in the other two, it becomes disk-like. The kinetic energy of the electrons can then be written as $E = p^2/2m^*$, resembling the kinetic energy of a free particle (p = momentum, m = mass), with the exception that the mass has been replaced by the effective mass m^*. The effective mass indicates the ease with which an electron can be moved by the electric field. If the electrons are easy to move, the conductivity is high. Easy motion is described by a small effective mass (small inertia) and p must also be small to keep E constant. If it is infinitely difficult to

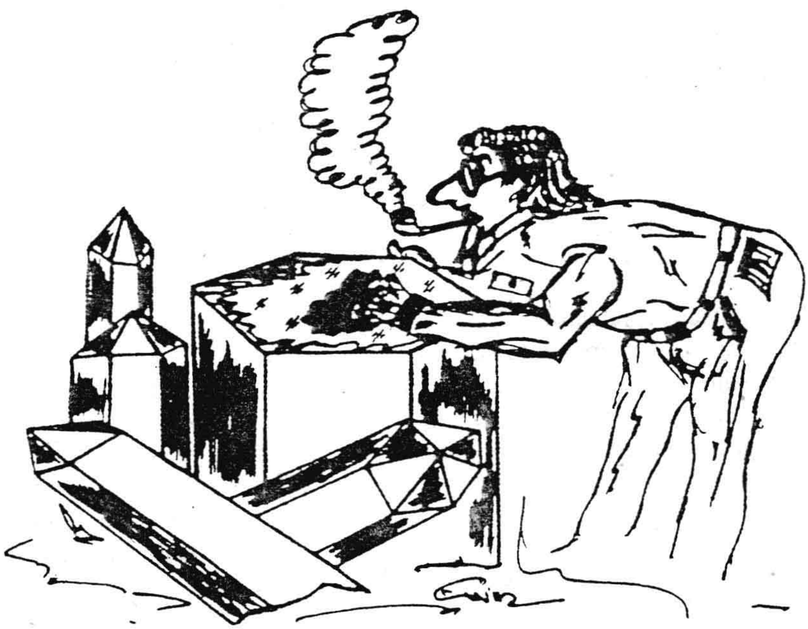

Figure 1–5: Crystal surfaces are excellent two-dimensional systems. The man above tries to improve the crystal face by mechanical polishing. The qualities achieved by this method are not sufficient for surface science. Surface scientists cleave their samples under ultrahigh vacuum conditions and use freshly cleaved surfaces for their experiments.

move an electron in a specific direction, the effective mass will become infinitely large in this direction and the Fermi surface will be infinitely far away. However, the extension of the Fermi surface is restricted: if the Fermi surface becomes too large in any direction it will merge with the Fermi surface generated by the neighboring chain ("next Brillouin zone", in proper solid-state physics terminology). This merging "opens" the Fermi surface, similar to a soap bubble linking with another bubble (Figure 1–6).