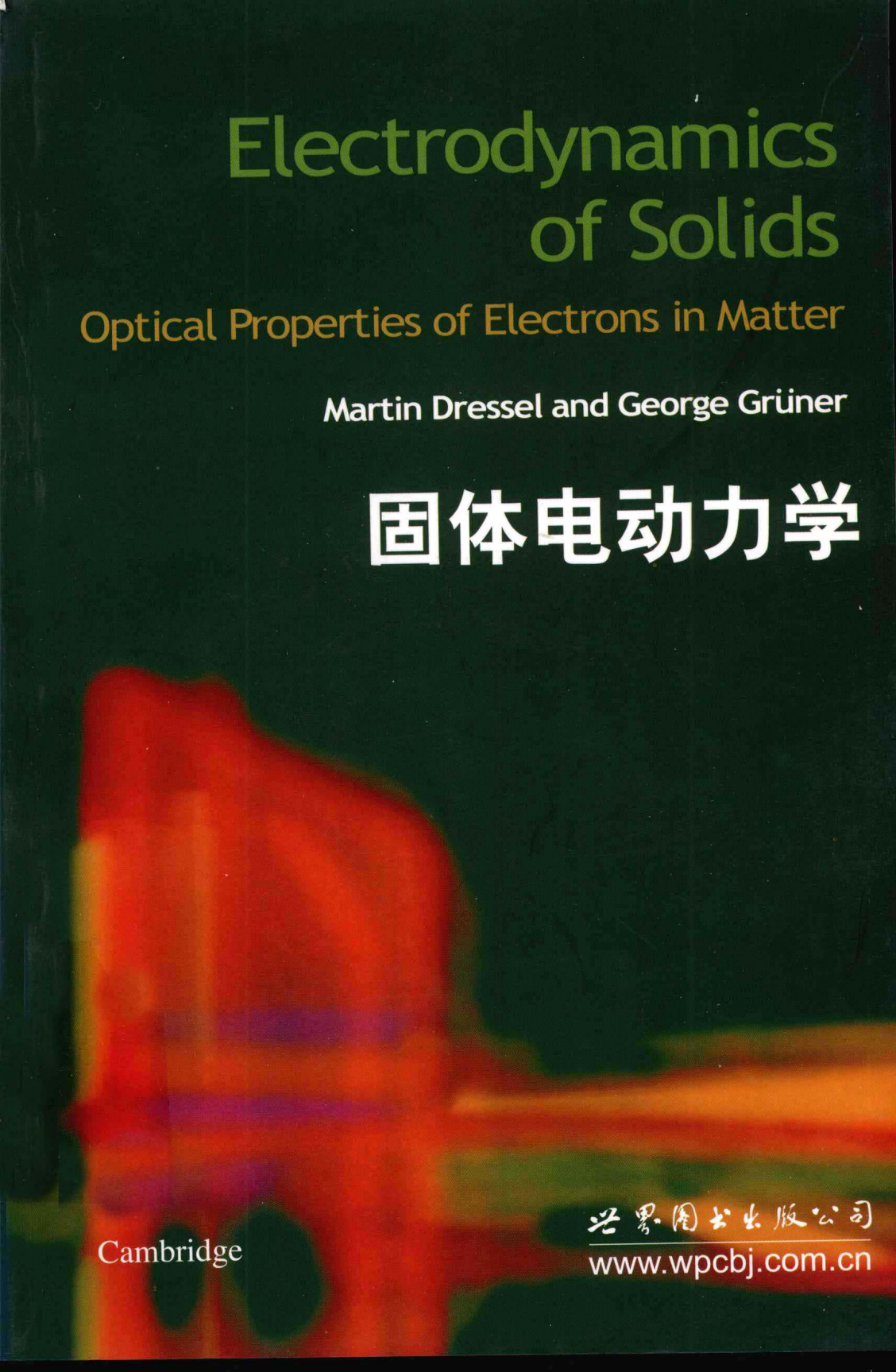
Electrodynamics of Solids

Optical Properties of Electrons in Matter

Martin Dressel and George Grüner

固体电动力学



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Preface

This book has its origins in a set of lecture notes, assembled at UCLA for a graduate course on the optical studies of solids. In preparing the course it soon became apparent that a modern, up to date summary of the field is not available. More than a quarter of a century has elapsed since the book by Wooten: Optical Properties of Solids – and also several monographs – appeared in print. The progress in optical studies of materials, in methodology, experiments and theory has been substantial, and optical studies (often in combination with other methods) have made definite contributions to and their marks in several areas of solid state physics. There appeared to be a clear need for a summary of the state of affairs – even if with a somewhat limited scope.

Our intention was to summarize those aspects of the optical studies which have by now earned their well deserved place in various fields of condensed matter physics, and, at the same time, to bring forth those areas of research which are at the focus of current attention, where unresolved issues abound. Prepared by experimentalists, the rigors of formalism are avoided. Instead, the aim was to reflect upon the fact that the subject matter is much like other fields of solid state physics where progress is made by consulting both theory and experiment, and invariably by choosing the technique which is most appropriate.

'A treatise expounds, a textbook explains', said John Ziman, and by this yardstick the reader holds in her or his hands a combination of both. In writing the book, we have in mind a graduate student as the most likely audience, and also those not necessarily choosing this particular branch of science but working in related fields. A number of references are quoted throughout the book, these should be consulted for a more thorough or rigorous discussion, for deeper insight or more exhaustive experimental results.

There are limits of what can be covered: choices have to be made. The book focuses on 'mainstream' optics, and on subjects which form part of what could be termed as one of the main themes of solid state physics: the electrodynamics or

(to choose a more conventional term) the optical properties of electrons in matter. While we believe this aspect of optical studies will flourish in future years, it is also evolving both as far as the techniques and subject matter are concerned. Near-field optical spectroscopy, and optical methods with femtosecond resolution are just two emerging fields, not discussed here; there is no mention of the optical properties of nanostructures, and biological materials – just to pick a few examples of current and future interest.

Writing a book is not much different from raising a child. The project is abandoned with frustration several times along the way, only to be resumed again and again, in the hope that the effort of this (often thankless) enterprise is, finally, not in vain. Only time will tell whether this is indeed the case.

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Feedback from many people was essential in our attempts to improve, correct, and clarify this book, for this we are grateful to the students who took the course. Wolfgang Strohmaier prepared the figures. The Alexander von Humboldt and the Guggenheim Foundations have provided generous support; without such support the book could not have been completed.

Finally we thank those who shared our lives while this task was being completed, Annette, Dani, Dora, and Maria.

Contents

1

Introduction

Ever since Euclid, the interaction of light with matter has aroused interest – at least among poets, painters, and physicists. This interest stems not so much from our curiosity about materials themselves, but rather to applications, should it be the exploration of distant stars, the burning of ships of ill intent, or the discovery of new paint pigments.

It was only with the advent of solid state physics about a century ago that this interaction was used to explore the properties of materials in depth. As in the field of atomic physics, in a short period of time optics has advanced to become a major tool of condensed matter physics in achieving this goal, with distinct advantages – and some disadvantages as well – when compared with other experimental tools.

The focus of this book is on optical spectroscopy, defined here as the information gained from the absorption, reflection, or transmission of electromagnetic radiation, including models which account for, or interpret, the experimental results. Together with other spectroscopic tools, notably photoelectron and electron energy loss spectroscopy, and Raman together with Brillouin scattering, optics primarily measures charge excitations, and, because of the speed of light exceeding substantially the velocities of various excitations in solids, explores in most cases the $\Delta\mathbf{q} = 0$ limit. While this is a disadvantage, it is amply compensated for by the enormous spectral range which can be explored; this range extends from well below to well above the energies of various single-particle and collective excitations.

The interaction of radiation with matter is way too complex to be covered by a single book; so certain limitations have to be made. The response of a solid at position $\mathbf{r}$ and time t to an electric field $\mathbf{E}(\mathbf{r}', t')$ at position $\mathbf{r}'$ and time t' can be written as

$$D_i(\mathbf{r}, t) = \int\int \bar{\bar{\epsilon}}_{ij}(\mathbf{r}, \mathbf{r}', t, t') E_j(\mathbf{r}', t')\, \mathrm{d}t'\, \mathrm{d}\mathbf{r}' \qquad (1.0.1)$$

where i and j refer to the components of the electric field $\mathbf{E}$ and displacement field $\mathbf{D}$; thus $\bar{\bar{\epsilon}}_{ij}$ is the so-called dielectric tensor. For homogeneous solids, the response depends only on $\mathbf{r} - \mathbf{r}'$ (while time is obviously a continuous variable), and Eq. (1.0.1) is reduced to

$$D_i(\mathbf{r}, t) = \int\int \bar{\bar{\epsilon}}_{ij}(\mathbf{r} - \mathbf{r}', t - t') E_j(\mathbf{r}', t')\, \mathrm{d}t'\, \mathrm{d}\mathbf{r}' \quad . \tag{1.0.2}$$

We further assume linear response, thus the displacement vector $\mathbf{D}$ is proportional to the applied electric field $\mathbf{E}$. In the case of an alternating electric field of the form

$$\mathbf{E}(\mathbf{r}, t) = \mathbf{E}_0 \exp\{\mathrm{i}(\mathbf{q} \cdot \mathbf{r} - \omega t)\} \tag{1.0.3}$$

the response occurs at the same frequency as the frequency of the applied field with no higher harmonics. Fourier transform then gives

$$D_i(\mathbf{q}, \omega) = \bar{\bar{\epsilon}}_{ij}(\mathbf{q}, \omega) E_j(\mathbf{q}, \omega) \tag{1.0.4}$$

with the complex dielectric tensor assuming both a wavevector and frequency dependence. For $\bar{\bar{\epsilon}}_{ij}(\mathbf{r} - \mathbf{r}', t - t')$ real, the $\mathbf{q}$ and ω dependent dielectric tensor obeys the following relation:

$$\bar{\bar{\epsilon}}_{ij}(\mathbf{r} - \mathbf{r}', t - t') = \bar{\bar{\epsilon}}^*_{ij}(\mathbf{r} - \mathbf{r}', t - t') \quad ,$$

where the star (*) refers to the complex conjugate. Only cubic lattices will be considered throughout most parts of the book, and then $\hat{\epsilon}$ is a scalar, complex quantity.

Of course, the response could equally well be described in terms of a current at position $\mathbf{r}$ and time t, and thus

$$J(\mathbf{r}, t) = \int\int \hat{\sigma}(\mathbf{r}, \mathbf{r}', t, t') E(\mathbf{r}', t')\, \mathrm{d}t'\, \mathrm{d}\mathbf{r}' \tag{1.0.5}$$

leading to a complex conductivity tensor $\hat{\sigma}(\mathbf{q}, \omega)$ in response to a sinusoidal time-varying electric field. The two response functions are related by

$$\hat{\epsilon}(\mathbf{q}, \omega) = 1 + \frac{4\pi \mathrm{i}}{\omega} \hat{\sigma}(\mathbf{q}, \omega) \quad ; \tag{1.0.6}$$

this follows from Maxwell's equations.

Except for a few cases we also assume that there is a local relationship between the electric field $\mathbf{E}(\mathbf{r}, t)$ and $\mathbf{D}(\mathbf{r}, t)$ and also $\mathbf{j}(\mathbf{r}, t)$, and while these quantities may display well defined spatial dependence, their spatial variation is identical; with

$$\frac{\mathbf{J}(\mathbf{r})}{\mathbf{E}(\mathbf{r})} = \hat{\sigma} \qquad \text{and} \qquad \frac{\mathbf{D}(\mathbf{r})}{\mathbf{E}(\mathbf{r})} = \hat{\epsilon} \tag{1.0.7}$$

two spatially independent quantities. This then means that the Fourier transforms

of $\hat{\epsilon}$ and $\hat{\sigma}$ do not have $\mathbf{q} \neq 0$ components. There are a few notable exceptions when some important length scales of the problem, such as the mean free path ℓ in metals or the coherence length ξ_0 in superconductors, are large and exceed the length scales set by the boundary problem at hand. The above limitations then reduce

$$\hat{\sigma}(\omega) = \sigma_1(\omega) + \mathrm{i}\sigma_2(\omega) \qquad \text{and} \qquad \hat{\epsilon}(\omega) = \epsilon_1(\omega) + \mathrm{i}\epsilon_2(\omega) \tag{1.0.8}$$

to scalar and $\mathbf{q}$ independent quantities, with the relationship between $\hat{\epsilon}$ and $\hat{\sigma}$ as given before. We will also limit ourselves to non-magnetic materials, and will assume that the magnetic permeability $\mu_1 = 1$ with the imaginary part $\mu_2 = 0$.

We will also make use of what is called the semiclassical approximation. The interaction of charge e_i with the radiation field is described as the Hamiltonian

$$\mathcal{H} = \frac{1}{2m} \sum_i \left[\mathbf{p}_i - \frac{e_i}{c} \mathbf{A}(\mathbf{r}_i) \right]^2 \quad , \tag{1.0.9}$$

and while the electronic states will be described by appropriate first and second quantization, the vector potential $\mathbf{A}$ will be assumed to represent a classical field. We will also assume the so-called Coulomb gauge, by imposing a condition

$$\nabla \cdot \mathbf{A} = 0 \quad ; \tag{1.0.10}$$

this then implies that $\mathbf{A}$ has only transverse components, perpendicular to the wavevector $\mathbf{q}$.

Of course one cannot do justice to all the various interesting effects which arise in the different forms of condensed matter – certain selections have to be made, this being influenced by our prejudices. We cover what could loosely be called the electrodynamics of electron states in solids. As the subject of what can be termed electrodynamics is in fact the response of charges to electromagnetic fields, the above statement needs clarification. Throughout the book our main concern will be the optical properties of electrons in solids, and a short guide of the various states which may arise is in order.

In the absence of interaction with the underlying lattice, and also without electron–electron or electron–phonon interactions, we have a collection of free electrons obeying – at temperatures of interest – Fermi statistics, and this type of electron liquid is called a Fermi liquid. Interactions between electrons then lead to an interacting Fermi liquid, with the interactions leading to the renormalization of the quasi-particles, leaving, however, their character unchanged. Under certain circumstances, notably when the electron system is driven close to an instability, or when the electronic structure is highly anisotropic, this renormalized Fermi-liquid picture is not valid, and other types of quantum liquids are recovered. The – not too appealing – notion of non-Fermi liquids is usually adopted when deviations

from a Fermi liquid are found. In strictly one dimension (for example) the nature of the quantum liquid, called the Luttinger liquid, with all of its implications, is well known. Electron–phonon interactions also lead to a renormalized Fermi liquid.

If the interactions between the electrons or the electron–phonon interactions are of sufficient strength, or if the electronic structure is anisotropic, phase transitions to what can be termed electronic solids occur. As is usual for phase transitions, the ordered state has a broken symmetry, hence the name broken symmetry states of metals. For these states, which are called charge or spin density wave states, translational symmetry is broken and the electronic charge or spin density assumes a periodic variation – much like the periodic arrangement of atoms in a crystal. The superconducting state has a different, so-called broken gauge symmetry. Not surprisingly for these states, single-particle excitations have a gap – called the single-particle gap – a form of generalized rigidity. As expected for a phase transition, there are collective modes associated with the broken symmetry state which – as it turns out – couple directly to electromagnetic fields. In addition, for these states the order parameter is complex, with the phase directly related to the current and density fluctuations of the collective modes.

Disorder leads to a different type of breakdown of the Fermi liquid. With increasing disorder a transition to a non-conducting state where electron states are localized may occur. Such a transition, driven by an external parameter (ideally at $T = 0$ where only quantum fluctuations occur) and not by the temperature, is called a quantum phase transition, with the behavior near to the critical disorder described – in analogy to thermal phase transitions – by various critical exponents. This transition and the character of the insulating, electron glass state depend on whether electron–electron interactions are important or not. In the latter case we have a Fermi glass, and the former can be called a Coulomb glass, the two cases being distinguished by temperature and frequency dependent excitations governed by different exponents, reflecting the presence or absence of Coulomb gaps.

A different set of states and properties arises when the underlying periodic lattice leads to full and empty bands, thus to semiconducting or insulating behavior. In this case, the essential features of the band structure can be tested by optical experiments. States beyond the single-electron picture, such as excitons, and also impurity states are essential features here. All this follows from the fundamental assumption about lattice periodicity and the validity of Bloch's theorem. When this is not relevant, as is the case for amorphous semiconductors, localized states with a certain amount of short range order are responsible for the optical properties.

The response of these states to an electromagnetic field leads to dissipation, and this is related to the fluctuations which arise in the absence of driving fields. The relevant fluctuations are expressed in terms of the current–current

or density–density correlation functions, related to the response through the celebrated fluctuation-dissipation theorem. The correlation functions in question can be derived using an appropriate Hamiltonian which accounts for the essential features of the particular electron state in question. These correlations reflect and the dissipation occurs through the elementary excitations. Single-particle excitations, the excitation of the individual quasi-particles, may be the source of the dissipation, together with the collective modes which involve the cooperative motion of the entire system governed by the global interaction between the particles. Electron–hole excitations in a metal are examples of the former, plasmons and the response of the broken symmetry ground state are examples of the latter. As a rule, these excitations are described in the momentum space by assuming extended states and excitations with well defined momenta. Such excitations may still exist in the case of a collection of localized states; here, however, the excitations do not have well defined momenta and thus restrictions associated with momentum conservation do not apply.

Other subjects, interesting in their own right, such as optical phonons, dielectrics, color centers (to name just a few) are neglected; and we do not discuss charge excitations in insulators – vast subjects with interesting properties. Also we do not discuss the important topic of magneto-optics or magneto-transport phenomena, which occur when both electric and magnetic fields are applied.

The organization of the book is as follows: underlying theory, techniques, and experimental results are discussed as three, inter-relating parts of the same endeavor. In Part 1 we start with the necessary preliminaries: Maxwell's equations and the definition of the optical constants. This is followed by the summary of the propagation of light in the medium, and then by the discussion of phenomena which occur at an interface; this finally brings us to the optical parameters which are measured by experiment. The three remaining chapters of Part 1 deal with the optical properties of metals, semiconductors, and the so-called broken symmetry states of metals. Only simple metals and semiconductors are dealt with here, and only the conventional broken symmetry states (such as BCS superconductors) will be covered in the so-called weak coupling limit. In these three chapters three different effects are dominant: dynamics of quasi-free electrons, absorption due to interband processes, and collective phenomena.

In Part 2 the experimental techniques are summarized, with an attempt to bring out common features of the methods which have been applied at vastly different spectral ranges. Here important similarities exist, but there are some important differences as well. There are three spectroscopic principles of how the response in a wide frequency range can be obtained: measurements can be performed in the frequency domain, the time domain, or by Fourier transform technique. There are also different ways in which the radiation can interact with the material studied: