

Manfred Fiebig

Nonlinear Optics on Ferroic Materials



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For Gertrud – The most important chapter of this story

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Preface

This book brings three fields of physics together, namely symmetry, spontaneous long-range ('ferroic') order, and nonlinear (in its response to the light field) laser optics. Nonlinear optics on ferroic materials is a subject that came to life in the early 1990s. Since then, it has been developing with remarkable success. Despite this interest, there appears to be no comprehensive presentation of the topic in book format. In fact, even review articles on the subject are scarce and generally focus on a single type of ferroic order or other selected aspects. Writing a book on nonlinear optics on ferroic materials therefore seems to be both timely and urgent.

As an introductory work, it aims at as wide a circle of readers as possible. This is a necessity because with symmetry, ferroic order, and laser optics, the book combines three vastly different areas, and the fewest readers will have a background in all of them. A prerequisite of this book is therefore the creation of a common perspective on the three subjects and, thus, of a common terminology to present them. This may tempt specialists in the respective fields to grumble about the inappropriate choice of language. The reward, however, is mutual understanding with the prospect of building bridges and joining forces in solving a timely problem. Given the current world situation, this seems to be more important than ever.

The introductions on symmetry, ferroic order, and nonlinear optics in Chapter 1 are written such that graduate students in the natural or engineering sciences should be able to follow and encourage them to read on. The book should also be quite useful for those who are looking for a topic for their doctoral thesis or the academic career that builds on it. Its approach is interdisciplinary, it points out numerous blank spots in the field, and research on these has a good chance of leading to novel, important insights.

Most of all, I would like to have readers fun in reading this work. I seriously hope that they feel some of the excitement I experienced while working in the field of nonlinear optics on ferroic materials and also in writing this book. Time to begin! So: Yeah – Is everything in place?

Zürich September 2023 Manfred Fiebig

Acknowledgements

(After a near-fatal attack)

C/E JOHANN: Electric motor fixed. Main pump fixed. Water can be pumped into tanks, then blown out with compressed air. Compass ready. Sonar ready.

LT. WERNER: Good, chief! Good. Good. - Take a rest now.

LT. WERNER: You just have to have good people. Good people!

The Boat, Wolfgang Petersen, Germany (1981)

This work would not have been possible without invaluable contributions from many different sides. First of all, I would like to thank my mentors who have influenced me both scientifically and through their person as well as with the attitude according to which they treat both research and researchers. They are Dietmar Fröhlich, who opened up the fascinating worlds of nonlinear optics and lasers to me, Roman Pisarev, who taught me about the wonders of magnetism and time reversal, Kenjiro Miyano, who was very tolerant of the peculiarities of a young strong-willed postdoc buzzing around his labs, and finally Thomas Elsässer, who gave me unimagined freedom in letting me develop my scientific ways under his roof. I also appreciate occasional kicks by Burkard Hillebrands, Yoshinori Tokura, Hans Schmid, and Ramamoorthy Ramesh in the right direction. I thank the institutions that hosted me over the years: The Technical University of Dortmund, The University of Tokyo - Todai, the Max Born Institute, The Rhenish Friedrich Wilhelm University of Bonn, and the Swiss Federal Institute of Technology in Zurich - ETH Zurich. I furthermore acknowledge financial support by the German Research Council (DFG), the Japan Science and Technology Corporation (JST), the Swiss National Science Foundation (SNSF), and the European Research Council (ERC).

Science can only be truly successful and enjoyable if the people working together on a daily basis are not just colleagues but, at least to some extent, friends. Here, I would like to thank Nicola Spalding in particular. For 20 years now, I have enjoyed our tossing around of more or less crazy ideas (with replaying the Big Bang and teleportation certainly on the 'more' side). Discussions with Nicola helped to stay

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Most of my own findings in this book exist only because I have had the privilege of heading a group of really fantastic people over the years. Here, Thomas Lottermoser has accompanied me for the longest time. With his calm and thoughtful manner, he provided the necessary counterpoint to my rather spontaneous and impulsive ideas. His knowledge of human nature was invaluable in the search for new team members. Morgan Trassin, on the other hand, represents the scientific counterpart of my activities. He understands ferroelectrics and taught me to use the word 'device' without getting a hiccup. In short, he complements me in those areas of research where I am not very gifted, and I greatly enjoy our daily banter about it. I am indebted to Dennis Meier, Mads Weber, and Shovon Pal, who entered the group on a postdoctoral position but were doing so much more than just great research. As Junior Group Leaders they left their unmistakable mark on the 'Laboratory for Multifunctional Ferroic Materials'. I cannot thank enough the team of wonderful doctoral and postdoctoral researchers I have been able to work with over the years. They are at the forefront of experiments and simulations that define my own success. More than anything, I enjoy the daily encounters with the FERROICS: a blend of individuals from 15 or so countries from all over the world. I admire their courage to make the challenging leap into a sometimes completely foreign environment, motivated by the urge to follow their talent and their cultural curiosity. They are the best proof that it is possible to live in peace with one another if only one wants to, and how enriching and productive this is for everybody.

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I would also like to acknowledge a number of locations for providing the recreative environment and counterbalance after hours at the institute. These are Tokyo, Berlin (yes, Morgan!), and Zurich with all its great cinemas, as well as, in an odd way, Boston. I must have spent months in the latter, always around the end of November, as attendee of the incessantly productive meetings of the Materials Research Society. I secretly wonder if there is a Boston without cold, darkness, and Christmas carols. In addition, I thank Dieter Kosslick and his Berlinale. This fantastic and totally unpretentious film festival offers fascinating insights into the world, and at least one hire in my group is in part due to curiosity about a country that arose in me because it frequently produces the best festival films.

My greatest thanks go to my friends and family. Here, I thank Dirk and Kerstin, dear friends since the first semester in Dortmund. They took care that I have that other knowledge that is indispensable for becoming a respected physicist: 'The Hitchhiker's Guide to the Galaxy' and the 'Tales of Pirx the Pilot', to name just two. And thanks for your bits and bytes when booking the Berlinale tickets! I cannot thank my parents enough who supported me unconditionally in my choice of career and encouraged me in it, especially in difficult times. Unfortunately, my father is no longer with us to hold the printed result of this support in his hands, but I hope that my mother will enjoy it for herself and in his place. I also thank my sister and her family. They support me by their interest in the wonders of nature. It has encouraged me to always be able to explain what I do to lay people so they can get an idea of what I spend taxpayers' money on. I wrote Chapter 1 for Elke, Frank, and Lili-Marie in particular. Last but not least, I thank Gertrud, the most important person in my life. She had to endure not only my curses about things not working but also all the relocations that sometimes went to places that were only among the second best. It is a great fortune that Gertrud pursues a profession that made these moves possible for her at all. Still, she always had to give up something and leave dear things behind when we went to a new place. How can I ever make up for that? I especially thank Gertrud for our two and a half years of Japan adventures and for her optimism and good humour, which I cannot muster so easily, and certainly not before 10 in the morning. For the time at your side, I thank you from the bottom of my heart.

Manfred Fiebig

A Preview of the Subject of the Book

MARIANNE: Forgive me, I'd hate to be in your place.

 $H \pm LOTINE$: We are in the same place. Exactly the same place. Come here. Come. Step closer. Look. If you look at me, who do I look at?

Portrait of a Lady on Fire, Céline Sciamma, France (2019)

1.1 Symmetry Considerations

Almost everyone can relate to the concept of *symmetry*. People usually associate symmetry with something that looks the same on the right- and left-hand side of some centre. Often, symmetry is associated with beauty, whereas asymmetry is considered as unpleasant. On the other hand, asymmetry may be used to create tension and make an object or image appear as interesting where symmetry might convey an impression of dullness. Most people also have an intuitive understanding of the consequences of symmetry. Imagine a picture of a symmetric object, say, of a human body, in which the right half is the (approximate) mirror image of the left half. Even someone who is not an orthopaedic will assume that the arrangement of bones and muscles in foot on the left is a mirror image of the arrangement of bones and muscles in the foot on the right. Here, a correct transfer from the symmetry of the larger object on the symmetry of its hidden components is made. Symmetry obviously allows us to make conclusions about the structure of objects even if we do not understand their composition and functionality in detail.

This principle can be extended to impressive lengths. Imagine an intelligent alien life form that is presented with pictures taken on Earth, as in Figure 1.1, showing a tree and a cow from above. Those aliens may have no idea what these objects represent. They will notice, however, that the tree thing looks roughly the same in all directions. So, whatever that object represents, it is probably rooted to the ground because if it were consciously mobile, it would most likely have a sort of front end in the direction in which it moves in order to detect what lies ahead. Because of this particular purpose, this front end is expected to look different from the rest of its body.

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Figure 1.1 The potential of symmetry analysis. (a) Deciduous tree from above. There is no direction here that stands out above another, see the double arrows. In consequence, rotation around the centre does not change the general appearance of the tree. With the lack of a built-in direction it is expected that trees do not move but rather stay rooted to the ground. (b) Cow from above. With respect to the long axis there is a clear difference between the two ends of the cow. It can be interpreted as a direction built into the animal (arrow), which eventually indicates its direction of motion. With respect to its sides, there is no direction that would distinguish left from right, so no motion along this axis is expected, as indicated by the double arrow.

This is the very concept applying to the cow thing. It does not look the same in all directions. Specifically, with respect to its long axis, one end is different from its opposite. Presumably, this therefore indicates the direction of motion of the object. A sentient mobile being needs to see what lies ahead but not what lies behind, so that the two ends will look different. In contrast, the long sides of the cow thing look about the same. There is no preferred direction here, and so, these sides will not be related to the direction of the movement.

Hence, from the rotational symmetry of the tree and its absence in the case of the cow, the alien life form concludes that not only the latter is consciously mobile but also the former is rooted to the ground. The aliens can also suspect that the cow represents the more intelligent form of life as it controls its direction of motion. That is a lot of knowledge about two systems whose meaning and inner structure are completely unknown to its observer, and all of it is derived from symmetry. Furthermore, it is the absence rather than the presence of the symmetry that tells something about the structure and function of the associated object, here exemplified by the directional structure of the cow that gives away its conscious mobility by breaking the rotational symmetry exhibited by the immobile tree.

In the context of this book, we deal with materials whose atomic structure and electronic interactions we often do not know in detail. Therefore, symmetry is our most powerful tool in extracting the structure and function of these materials, very much in the same way as we have done with Figure 1.1. We consequently employ experimental methods that are strongly rooted in symmetry for our investigations. Two of the symmetry operations we consider have already been mentioned, namely rotations and mirror operations. Both describe the reorientation of an object in the three-dimensional space we are living in, but they do not change the shape of the object, for example by stretching it. Accordingly, we only consider symmetry operations that preserve the length of an object in each direction. These are translations from one point in space to another, rotations around a certain axis, and mirror operations on a designated point or plane. Reversing the direction of the passage of time also does not change the length of an object and is therefore considered. This might seem odd since the direction of time cannot be changed. Time reversal makes sense, however, when we discuss an electric current flowing from location A to location B. Reversing the direction of time converts it into a current flowing from B to A, and considering if a material remains unchanged or not under such an electric-current reversal is not unphysical. In fact, it will turn out that time-reversal symmetry is crucial for describing magnetically ordered systems because magnetic fields are classically generated by electric currents.

1.2 Ferroic Materials

Almost everyone can also relate to *magnetism*. It is exhibited by certain objects called magnets that attract iron, which is useful because it makes postcards stick to the fridge. For the attentive observer, magnetism can be found in almost all areas of daily life. Electric motors, current generators, sensors, computer hard disks, and compasses are among the objects usually associated with it. In fact, in a typical household, hundreds of magnets can be found, with more than 100 built into a car alone. The fact that magnetism has been with humankind for at least 2500 years makes us forget that it is one of the most mysterious phenomena of nature. It acts without carrier medium across space, a concept captured, yet not explained, by the introduction of a magnetic field. Magnetic fields are generated by electric currents, but no such current is found in a rod magnet. Instead, we had to introduce the notion of a quantum-mechanical spin as its source, but again, this mostly represents a description rather than a true explanation. Few people realise that with a magnet for less than a euro, they have quantum mechanics in its purest form in their hands.

Readers may remember from school that matter is made up of atoms that are themselves small magnets as depicted in Figure 1.2a. If all these point in the same direction, the very small fields of a very large number of atomic magnets, called magnetic moments, add up to yield the characteristic magnetic field surrounding a magnet, as sketched in Figure 1.2b,d. This picture already leads to one of the most important properties of a magnet. It represents a form of order in a material that is not enforced by some external influence but arises spontaneously below a certain temperature. There is field that can act on a magnet and orient it in a certain direction, such as Earth's magnetic field in the case of a compass needle.

Eventually, it turned out that magnetism is only one of several forms of order that are associated with a surrounding field and arise spontaneously in a material below a certain temperature. The generic term *ferroic* was introduced to tag these. It refers to the magnetic order of iron, but as a prefix it indicates ordered states as described

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Figure 1.2 Magnetic and electric order of materials. (a) Atoms in a crystal representing minuscule magnets. In most materials these so-called magnetic moments point in random directions so that the total magnetic fields cancel out. (b) Spontaneous order may occur, where all the atomic magnets point in the same direction. The magnetic moments of such a ferromagnet add up to reveal its characteristic magnetic field. (c) Spontaneous alternating arrangement of the magnetic moments still represents an ordered state, yet without a magnetic field because of the cancellation for the oppositely oriented magnetic moments. A material of this type is denominated as antiferromagnet. (d) Magnetic field surrounding the ordered magnetic moments of a ferromagnet. (e) Electric field surrounding the ordered electric dipoles of a ferroelectric. The lines in (d) and (e) indicate the direction of the field. Despite the very similar field distribution, the origins of the ferromagnetic and ferroelectric orders are quite different.

above in any type of material, even if iron is not involved. Along with the introduction of this prefix, the somewhat unspecific term 'magnetic' was replaced by *ferromagnetic* in order to distinguish it from other forms of magnetic order. Note that in line with what we have just said, nickel also counts as ferromagnet rather than being denominated as 'niccolomagnet'. Chemical elements that are ferromagnetic at room temperature are iron, cobalt, and nickel, and certain rare metals are coming close.

Almost exactly a century ago, it was recognised that matter can spontaneously order itself electrically. A crude analogy to the atomic magnets mentioned above would be that of minuscule batteries, formed, for example by a pair of atoms of which one is positively and one is negatively charged. If all these pairs, called electric dipoles, spontaneously point in the same direction, we have a material that is electrically ordered and surrounded by an electric field as shown in Figure 1.2e that can attract charged particles. A material of this type would be called *ferroelectric*. Although few people are aware of this property, ferroelectrics play a not inconsiderable role in our daily lives. Sonar and certain loudspeakers, buzzers, or sensors are based on ferroelectrics, and even computer components based on ferroelectric rather than ferromagnetic memory are in operation.

Finally, about half a century ago it was found that certain materials can deform spontaneously, which can be associated with a mechanical strain field. This property

is denominated as *ferroelastic*, and it concludes the set of currently fully established forms of ferroic order that nature can display.

In addition to the three types of ferroics we have just mentioned, there are a number of variants, which also play important roles in science and technology. Foremost, there are materials where the atomic magnetic moments are ordered in an alternating fashion. If for a specific atomic magnet the north pole is pointing up, it is the south pole for the next atom, then again the north pole, and so forth, see Figure 1.2c. This is a form of spontaneous order as stringent as in the case of ferromagnetism, but because half of the magnetic moments point in one and the other half in the opposite direction, there is no resulting magnetic field that would surround such an object. A material exhibiting this kind of order is denominated as antiferromagnetic. Metallic chromium and manganese are well-known materials that are antiferromagnets at room temperature. In terms of technological applications, a fieldless magnet appears to be quite useless because it is not much different from materials that are not ordered in the first place. This is not true, however. A ferromagnet brought into contact with an antiferromagnet may sense the order of the latter, and this influence can be used to improve the technological performance of the ferromagnet. This principle is used in the read-write heads of computer hard disks. Furthermore, antiferromagnetism is closely related to superconductivity, the lossless, and thus energy-saving and waste-heat-avoiding flow of an electric current.

Because of the absence of a magnetic field, there is no general agreement on which forms of magnetic order should be counted as antiferromagnetism and which ones should not. This ambiguity is quite astonishing considering how intensively and how long the magnetic properties of matter have been studied. When it comes to the antiferroic equivalents for electric and elastic order, the situation is even worse. A spontaneous alternating arrangement of electric dipoles might be called *antiferroelectric*, but whereas the ferro- and antiferromagnetism are often associated with opposite signs of the same quantum-mechanical interaction, such a connection cannot be drawn in the case of antiferroelectricity. For this reason, the definition of an antiferroelectric is not only even more ambiguous than that of an antiferromagnet, but some scientists even doubt whether introducing the concept of antiferroelectricity makes sense at all. The situation is not better in relation to *antiferroelastic* materials.

We thus find ourselves in a rather unexpected situation. Ferromagnetism has been known to humankind for millennia, is known to almost everyone, is of enormous technical importance, and is well researched. The concept of ferroic order at large, however, is not very well defined in certain important aspects. In fact, the first proposition of an overarching concept for characterising it was only made in 1970 [1]. That approach was largely based on the symmetry change that occurs when the ferroic state is formed. A more comprehensive concept that included not only symmetry but also a number of phenomenological properties from physics and materials science was only introduced in the year 2000 [2]. What unites these two approaches is

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that they are based on the involvement of a very large number of atoms. Interactions on the level of the individual atoms that drive the spontaneous order are not part of the definition of a ferroic state. In the case of ferromagnetism, this is often forgotten. It is usually associated with a specific quantum-mechanical correlation between atoms, but there are manifestations of ferromagnetic order that are driven by other interactions.

As we have seen, the research field of ferroic materials is still in the midst of development, with a number of construction sites at key points. Questions of major interest are:

- Are there forms of ferroic order other than ferromagnetism, ferroelectricity, and ferroelasticity, the three established manifestations?
- What happens if more than one type of ferroic order is present in the same material, a constellation we denominate as *multiferroic*?
- How can we remove the existing ambiguities surrounding the concept of ferroic order?

In this book, we address these issues and propose new concepts, methods, and materials that we hope will advance the field of ferroics in some of its central aspects.

1.3 Laser Optics

Finally, almost everyone knows lasers and can associate the term *optics* with something involving light. In the combination of the two terms, people would generally imagine a source of intense light, where the latter is sent through transparent media such as microscopes and camera lenses, possibly in order to obtain a particularly bright image of an object illuminated with the laser radiation. In fact, this is exactly what we are planning to do here. Humans are ocular animals; the majority of information is received through the eye. Using a laser instead of a light bulb or the sun also permits us to see hitherto inaccessible aspects of an object because lasers represent not only a very bright but also a very clean source of light.

As in the case of (ferro-)magnets, there are some very surprising aspects about lasers that are not known to the majority of people. Similar to magnets, lasers are very quantum-mechanical objects. Coercing a material into emitting an intense, directed light beam can only be understood by resorting to the odd world of atoms where objects can appear as both a particle and a wave. A simple laser pointer can be bought and used by everyone and costs less than 10 euros, which makes us forget that it took until about 1960 to bring physics and technology together and demonstrate laser emission for the first time with a device as sketched in Figure 1.3a [3]. Furthermore, even though lasers are considered as an extremely intense source of light, capable of damaging the eye, they are in fact not very powerful. Some of the most intense laboratory lasers emit light of no more than about 10 W. The weakest vintage light bulbs used in households emit at least 25 W, and even LED light bulbs of 10 W are not particularly bright.



Figure 1.3 Nonlinear optical processes with lasers. (a) Design of the ruby laser used for the first demonstration of laser emission in 1960 [3]. A ruby crystal is optically excited with light from a flash lamp and driven to emit directed visible and very 'clean' deep red light with the help of two parallel mirrors. (b) First demonstration of a nonlinear optical process in the visible range. A quartz crystal is irradiated with the deep red light from a ruby laser (wavelength λ of 694 nm) to produce ultraviolet light at half the wavelength. The numbers indicate $\lambda/10$. The light was detected with a chemical film that is blackened by the incident laser light (big blotch) and the much weaker emission at half the wavelength (arrow). It is a curiosity of this landmark publication that the actual data point (arrow) is not visible. It was erased by the journal staff as an alleged dust particle when the figure was processed for publication. Source: (a) Reproduced with permission from Yadav [4]. (b) Reproduced with permission from Franken et al. [5]/with permission of American Physical Society.

The exceptional intensity associated with laser light comes about in two ways. First, the laser light is highly directed, whereas a light bulb emits its radiation in all directions. At the same emitted power, a laser beam of 4 mm diameter at a distance of 1 m from the laser is a million times as intense with respect to the area it illuminates than a light bulb. Second, lasers often emit light pulses rather than continuous radiation. Hence, the emission is 'compressed' into a very short time bracket, whereas the laser is 'off' during the rest of the time. While the emission is taking place, it is therefore much stronger than if the emission was occurring in a continuous way. If the two types of pulsed lasers we consider in the context of this book were operated all the year round without interruption, they would only emit light for an integrated time of 10 s and 10 ms, respectively.

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Apart from its unsurpassed intensity, laser light is also very clean in the sense that it has a very well-defined colour and thus wavelength, unlike light bulbs or the sun, which emit a broad distribution of wavelengths interpreted by the eye as white. In addition, the laser light wave forms a very even wave pattern, such as in the case of a rock thrown into a calm lake as opposed to wind rippling its surface.

With the laser, we thus have an extremely intense and uniform light source that helps us to detect optical processes that are normally too weak to be observed. These are foremost processes, where the colour of the light changes when it interacts with a material. Typically, an object that is illuminated with light at a specific colour (as opposed to the white light emitted by the sun or a light bulb) scatters back light at exactly this wavelength. We can picture this scattering process in the way that the atoms of the material absorb an optical quantum, called photon, from the light field and emit it again after a while. The photon and its energy do not change in the process so that the colour of the light remains the same.

If the radiation is very intense, as when using a laser, it is possible that an atom absorbs two photons at once because they are so densely distributed. In the subsequent re-emission, however, only a single photon is typically generated, which then carries the energy of both of the two ingoing photons. The higher energy corresponds to a shorter wavelength and, hence, to a change in colour. Thus, an object illuminated with deep red laser light emits a little bit of deep blue light as well. The part of optics dealing with wavelength-shifting processes of this type is denominated as *nonlinear optics*.

It is quite striking how closely the foundation of the field of nonlinear optics is tied to the invention of the laser as the intense light source permitting us to detect nonlinear optical processes. The laser was introduced in 1960 [3], and the first report of a nonlinear optical process was published in 1961 [5], see Figure 1.3b. This rapid succession was possible because the theory for the simultaneous absorption of two photons had already been existing for 30 years, and only the appropriate tool for visualising it was missing [6]. By now, nonlinear optical processes have become very important in studying the structure and properties of materials. Since more photons and more wavelengths than in a conventional optical process are involved, nonlinear optics opens up access to a larger reservoir of information about a material. In addition, it allows researchers to literally 'see' this information, for example when taking photos of a sample using the light generated in a nonlinear optical process.

1.4 Creating the Trinity

In Sections 1.1–1.3, we have introduced three seemingly unrelated subjects. Symmetry has a proximity to mathematics, ferroic order refers to materials, and nonlinear laser optics deals with electromagnetic radiation fields. In the following discussion, we will see that these three so very different subjects are in fact perfectly made for one another. As we have explained, symmetry is a tool that enables us to make rather specific statements about systems whose inner structure and functioning are unknown to us. This makes it perfect for characterising and analysing ferroic systems because ferroic order is defined at the macroscopic level, that is disregarding the inner structure. In particular, for some of the lesser studied manifestations of ferroic order, we do not know the microscopic, atomic origin of the transition to spontaneous order.

All types of ferroic order break symmetries by definition, which may help us to develop a concept for ferroic order at large [1] and search for materials exhibiting novel types of ferroic order. Symmetry, or rather its loss, is also particularly well suited to describe materials exhibiting more than one type of ferroic order in the same phase.

In summary, symmetry can help us to find novel types of ferroic order, to explore systems with multiple manifestations of ferroic order, and to find overarching criteria helping us to overcome the existing ambiguities surrounding the concept of ferroic order.

While symmetry is our conceptual approach to exploring ferroic states of matter, nonlinear laser optics is the practical way to probe it. Just like matter, light as an electromagnetic radiation field has its characteristic symmetries. For example, an oscillating electric field as simple representation of a light wave would not look different if it is mirrored on the plane in which the oscillation occurs. This mirror operation thus is a symmetry operation with respect to the light field. In contrast, time reversal is not a symmetry operation because it would reverse the direction in which the light is propagating. One can therefore assume that light can address and thus probe a specific type of ferroic order if the symmetry of the light field is compatible with the symmetry of the ferroic state. The symmetry of the light field is controlled by setting its polarisation and direction of propagation. This makes polarisation-dependent optical spectroscopy the perfect tool for investigating ferroic materials because for both the experimental tool and the system to which it is applied, symmetry is the common ground.

The particular advantage of optical experiments is that we can expand from linear optics involving a single light field towards nonlinear optics, where multiple light fields are brought in connection, as described above. By combining the symmetries of these light fields in the appropriate way, the very specific symmetry configurations of a ferroic state can be addressed with high selectivity. This can even be used to the extent that in systems featuring multiple types of ferroic order, the respective ferroic states can be addressed selectively by different nonlinear optical experimental configurations. Specifically, in a multiferroic exhibiting magnetic and electric order at the same time, the coexistence and interaction of the two forms of order can thus be investigated. No other experimental technique permits this to the extent nonlinear optics does.

As we see, the combination of symmetry, ferroic order, and nonlinear optics with lasers can give us unprecedented access to one of the most fascinating classes of materials. The nonlinear optical properties of ferroics have been investigated since the invention of the laser. From then on, the field has been developing with remarkable success. Despite several decades of research, however, there is only a relatively small number of review articles on this subject, and these articles are mostly focused

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on selected aspects. In particular, there appears to be no monograph presenting a comprehensive view on nonlinear optics applied to ferroic materials. It is the purpose of the work at hand to change this.

1.5 Structure of this Book

The Part I of this book is devoted to the **basics** and presents self-contained introductions on symmetry, ferroic order, and nonlinear optics. Rather than summarising earlier literature on these well-covered fields, we focus on those aspects that are little considered in the existing literature or that are relevant in bringing the three subjects together. This part concludes with an intuitive example uniting the introductions on symmetry, ferroic order, and nonlinear optics in a single model compound. This example provides a first glimpse at the extraordinary power of applying nonlinear optics to the study of ferroic materials and reveals several properties in our model compound that are inaccessible with other characterisation techniques.

The Part II of this book makes the transition from basics to materials. It elaborates on the added value that results from combining the fields of symmetry, ferroic order, and nonlinear optics. In terms of materials science, 'ferroic' was mostly understood as 'magnetic' or rather 'ferromagnetic'. The contemporary search for novel multifunctional and so-called 'smart' materials has been shifting the emphasis towards other forms of long-range, potentially ferroic types of order. There are, however, very few techniques allowing us to study these. Here, nonlinear optics is an outstanding tool with unique degrees of freedom, such as spectral resolution (access to those electronic states and sublattices of a crystal involved in the emergence of ferroic order), spatial resolution (visualisation and manipulation of differently ordered regions), and time resolution (visualisation of dynamical processes down to the femtosecond range).

In Part III of this book, classes of ferroic materials of central interest to contemporary condensed-matter physics are explored. This includes multiferroics with magnetoelectric correlations as materials uniting magnetic and ferroelectric order. Here, the scope is to achieve control of magnetic properties by electric fields as a foundation in the design of novel and energy-efficient magnetic devices. We also discuss oxide-electronic materials with a special focus on ferroelectrics. With oxide electronics, we furthermore enter the realm of thin films, multilayers, and nanostructuring. Finally, a variety of material classes with forms of ordering other than ferroic are discussed. Their nonlinear optical characterisation is at its infancy, and our brief review may help to stimulate further investigations. The book concludes with an epilogue that leads to the inevitable realisation that our work can only be a first step into largely uncharted territory. The best imaginable success of this monograph would be to foster and guide the ongoing exploration of the field.

Part I

The Ingredients and Their Combination

2

Symmetry

CALDICOTT: Lucky some of you fellows understand English.

ENEMY OFFICER: Well, I was at Oxford.

CHARTERS: Oh, really - so was I. What year?

REDMAN: Hold on, this woman seems to be trying to say something. I don't understand the language; it may be important. Would you...?

(The enemy officer bows to listen. Redman hits him over the head with a chair.)

REDMAN: That's fixed him.

CHARTERS: What the blazes did you do that for?

REDMAN: I was at Cambridge.

The Lady Vanishes, Alfred Hitchcock, England (1938)

2.1 Describing Interactions in Condensed-Matter Systems

Let us assume that we apply an external perturbation to a chunk of material, and the material responds in some form. Say, we take a crystal and place it in a static electric field, and in return, the crystal deforms by getting a bit longer in one and a bit shorter in the other directions. This property is called the (converse) piezoelectric effect, and it is actually quite useful. For example, when we use the electric voltage to set an acoustic membrane in motion, we get a buzzer or a loudspeaker.

We can describe this piezoelectric effect in two ways. The first approach would be to do this phenomenologically, at the macroscopic level of our daily-life world. We describe our experiment by putting the electric field on one side of the equation and the resulting deformation on the other. In principle, each of the components of the electric-field vector **E** has an influence on each of the components of the second-rank strain tensor \hat{S} parameterising the deformation. This leads to

$$S_{ij} = \sum_{k=1}^{3} d_{ijk}^{\rm pe} E_k,$$
(2.1)

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where the third-rank tensor \hat{d}^{pe} mediates the piezoelectric coupling. Indices *i*, *j*, and *k* refer to the unit vectors defining the underlying coordinate system. From now on, it is implied that a sum as in Eq. (2.1) is executed over all doubly occurring indices so that the sigma sign is omitted from the equations.

Alternatively, we can describe the piezoelectric coupling *ab initio*, at the microscopic level of the electronic and ionic states and quantum-mechanical interactions of the material. Our unperturbed system is then described by a Hamilton operator with eigenfunctions that are populated according to a density matrix $\hat{\rho}_0$. At the time t' = 0, a perturbation, in our case the electric field, is applied. This changes the Hamilton operator and the eigenfunctions of our system until after some time a new equilibrium, in our case the strained state, is reached. If the perturbation is small, this response can be described by linear response theory [7]. In our case, it leads to

$$d_{ijk}^{\text{pe}} \propto \lim_{t \to \infty} \int_0^\infty \operatorname{tr}\left(\hat{\rho}_0\left[\hat{S}_{ij}(t), \hat{E}_k(t')\right]\right) dt'.$$
(2.2)

Both the electric field and the strain become operators. The trace in combination with the density matrix for the unperturbed system associates these to measurable values. The time t of the strain response must always be larger than the time t' of the strain-generating electric field in order to retain causality.

So far, we have described and parameterised the piezoelectric effect on different levels, but we have not explained anything. Nevertheless, we have gained a lot. We have realised that we can divide the treatment of the piezoelectric effect into two entirely separate steps, represented by Eqs. (2.1) and (2.2), respectively. Equation (2.1) permits us to quantify the piezoelectric effect and work with it. At this point, we do not have to care about the physical origin of the effect because we have disposed of this discussion by shifting it into Eq. (2.2). In many cases, we can omit the discussion entirely because for building loudspeakers, an understanding of the sources of the piezoelectric coupling is usually not required.

The real power of the separation of physical effects into the macroscopic and the microscopic levels is that despite our complete ignorance about the physical sources of an effect its treatment at the macroscopic level already allows us to reach surprisingly detailed conclusions about these sources. The key to this is symmetry. Its significance lies in the fact that the symmetry of a material in its ground state must be reflected in the transformation behaviour of each of its measurable physical properties. This fundamental relation, known as the *Neumann principle* [8, 9], combines the structure of a material with its behaviour. Thus, when describing a macroscopic physical property by a tensor as in Eq. (2.1), then according to the Neumann principle, the application of any of the symmetry operations characterising a material must not change the components of this tensor. From this invariance follows a set of linear transformations in the tensor components. The solution of this set of equations provides statements about the structure of the tensor, especially about the relation between or zeroness of certain tensor components.

With some care, the Neumann principle can be applied bidirectionally. If we know the symmetry of a material, we can say if it permits the occurrence of the

piezoelectric effect. In turn, if we find that a material displays a piezoelectric effect, we can reach conclusions on the structure and symmetry of the system. We use the latter route in particular throughout this book and therefore need to develop a mathematical apparatus to work with symmetries. This leads us to group theory.

2.2 Introduction to Practical Group Theory

There is plenty of literature providing comprehensive introductions to group theory with a focus on the link between physical properties and mathematics [10], magnetic materials [11], semiconductors [12], molecules [13], or elementary particles [14]. Here, we restrict ourselves to an introduction of group theory on an applied level, as we require it for the description of crystalline ferroic materials and their investigation by nonlinear-optical techniques.

The system with the highest symmetry is the vacuum. It is homogeneous and isotropic in space and time. It is thus invariant under all space-time rotations SO(4) and translations $T_{4\infty}$ as well as under the discrete operations of spatial inversion \hat{I} , time reversal \hat{T} , and charge reversal \hat{C} . The combined set of operations forms the Poincaré group \mathcal{G}_0 , with

$$\mathcal{G}_0 = T_{4\infty} \otimes \mathrm{SO}(4) \otimes \hat{I} \otimes \hat{T} \otimes \hat{C}. \tag{2.3}$$

Here, a group G is an algebraic structure consisting of a set of elements a_i (with *i* as numerator) and an operation \otimes defining how to combine any two elements into a third element. As a group, this structure satisfies the following conditions:

- Closure. The result of the combination of any two elements of a group is an element of the group as well: a_i ⊗ a_i = a_k with a_{i,i,k} ∈ G.
- Associativity. Consecutive combinations of elements in \mathcal{G} can be grouped at will: $a_i \otimes (a_j \otimes a_k) = (a_i \otimes a_j) \otimes a_k$.
- Identity element. There exists a unique element 1 in *G* that, combined with any group element, does not change this element: $1 \otimes a_i = a_i$.
- **Inverse element.** For each element a_i of \mathcal{G} , there exists an inverse element a_i^{-1} such that their combination yields the identity element: $a_i \otimes a_i^{-1} = \mathbb{1}$.
- **Commutativity.** When two elements of *G* are combined, their sequence can be rearranged: $a_i \otimes a_j = a_j \otimes a_i$. This condition is not mandatory. Groups satisfying it are called *Abelian groups*.

In vacuum, translations and rotations are continuous symmetry operations, whereas spatial inversion, time reversal, and charge reversal are discrete. We can limit the space we are working in by splitting off charge reversal and temporal translations because they are not required when considering light–matter interaction in ferroic materials. This gets us to $G'_0 = T_{3\infty} \otimes SO(3) \otimes \hat{I} \otimes \hat{T}$, which is a subgroup of G_0 . Here, a group G_s is called a *subgroup* of G if both G_s and G are groups and follow the relation $G_s \subseteq G$. In the following section, we will see that it is often possible to restrict our working space even further and move on to the subgroups of G'_0 .

2.3 Crystals

A *crystal* is a solid material whose atoms, ions, or molecules are arranged in a periodic fashion in the three spatial directions. Its defining element is the *unit cell*, an imaginary box whose periodic repetition fills the entire space without gaps. For their classification, crystals are conceptually divided into the lattice and a basis. The *lattice* is a mathematical construct filling three-dimensional space with an infinite periodic arrangement of points. Three linearly independent so-called *lattice vectors*, say **a**, **b**, and **c**, span this lattice. Their linear combination according to $n_a \mathbf{a} + n_b \mathbf{b} + n_c \mathbf{c}$ with $n_{a,b,c}$ as integers defines the lattice points, so that the lattice exhibits a trivial translation symmetry with respect to its lattice vectors. There are only 14 different types of the so-called *Bravais lattices*, which differ from one another in terms of their symmetry properties. The Bravais lattices are in turn divided into seven crystal systems, namely triclinic, monoclinic, orthorhombic, tetragonal, trigonal, hexagonal, and cubic [9].

The *basis* is a group of atoms, ions, or molecules assigned to each lattice point. Since the assignment is the same for all points, the basis does not break the trivial translation symmetry of the lattice. A special case occurs when the basis of a crystal consists of a single atom. In this case, the positions of the lattice points and of the crystal atoms coincide, and it is tempting to give up the distinction between the lattice and the basis. This would not be correct, however, as the former remains to be a mathematical construct, whereas it is the basis that fills the crystal with life. The physical basis as defined here must not be confused with the crystallographic basis as the set of lattice vectors defining the crystal [15].

Since the positions of the basis atoms are not determined by integer or even rational multiples of the lattice vectors, the number of possible crystal structures is, in principle, infinite. Indeed, more than a million crystal structures and several thousand naturally occurring minerals forming crystals are known [16]. Nevertheless, all of these can be described by a well-defined, restricted set of crystallographic symmetries [9]. These symmetries are distinguished with respect to the unitary, that is length-conserving transformations in space and time, leaving them invariant. The different types of symmetry operations of this kind are introduced in Section 2.3.1. The classification of a crystal in terms of symmetry happens in two ways.

On the one hand, we distinguish between the sets of operations leaving the crystal structure as a whole invariant. This leads to the different types of symmetry groups introduced in Section 2.4.

On the other hand, the site symmetry of each basis atom at its specific position in the unit cell is considered. For example, let us consider a cubic unit cell as depicted in Figure 2.1. For an atom occupying the corner of a cubic unit cell defined by the cube edges as lattice vectors **a**, **b**, and **c** (Figure 2.1a), rotations around the cube's body diagonals by multiples of 120° are symmetry operations with respect to the position of the atom. There is one such position in each unit cell, composed of eight corner atoms, each of which protrudes 1/8 into the cubic cell. If the atom sits on a position halfway along the edge of the cubic unit cell (Figure 2.1b), the aforementioned rotations around the cube's body diagonals are no longer symmetry operations with respect to the position of the atom. Here, the site symmetry differs from



Figure 2.1 Site symmetry and the Wyckoff notation. For the same crystallographic symmetry, an atom placed at the corner of a cubic unit cell and an atom placed halfway along one of its edges experience different site symmetries. These are distinguished by the Wyckoff notation. (a) For an atom at the corner, a rotation by $\pm 120^{\circ}$ around the cubic body diagonal is a symmetry operation (label '3'). The corner position has the highest site symmetry (Wyckoff label 'a') and is associated with one atom per unit cell of this type (Wyckoff label '1'). The resulting Wyckoff position is 1a. (b) For an atom halfway along one of the cube edges, the rotation by $\pm 120^{\circ}$ around the cubic body diagonal is no longer a symmetry operation even though it remains a symmetry operation of the crystal as a whole. There are three independent displacements along lattice vectors (thick lines) **a**, **b**, or **c**, associated with three atoms per unit cell. This and the lower site symmetry lead to the designation as Wyckoff position 3d.

the symmetry of the crystallographic lattice as a whole. Since we can displace the atom along **a**, **b**, or **c**, we have three equivalent positions of this type per unit cell. The choice of three corresponds to the 12 edges of the cube, where each of the associated atoms protrudes 1/4 into the unit cell.

In the Wyckoff notation [15], a number and a letter are assigned to the position of each atom of the basis. Equal letters indicate all the positions in the unit cell having the same site symmetry. Enumeration according to a, b, c, ... occurs in the order of decreasing site symmetry of the atomic position. The preceding number indicates the number of symmetry-equivalent positions in the unit cell. In the previous example of a cubic crystal with atoms at the corners and halfway along the edges, the two locations correspond to the Wyckoff positions 1a and 3d, respectively. This also holds if both positions are occupied by the same type of atom. (Note that the b and c sites correspond to other displacements we have not discussed.)

2.3.1 Types of Symmetry Operations

2.3.1.1 Translations

A translation is a geometric transformation τ that moves every point **r** of a space by the same distance in a given direction. In crystals, we have to distinguish between translations by linear combinations of the lattice vectors and other three-dimensional translations. The lattice vectors define the space we are working in (the 'crystallographic vacuum'), and as such, translations between the lattice points are always symmetry operations. We therefore disregard this set of trivial symmetry operations henceforth.

In contrast, we have translations by fractions of the lattice vectors that, often in combinations with other transformations, are symmetry operations. These non-trivial translations depend on the exact positions of the basis atoms. For optical processes involving visible light, it is often a good approximation to disregard these non-trivial translations nonetheless. The displacements defining them do not exceed the expansion of the unit cell, and probing them at a wavelength of about 1000 unit cells leads to optical effects that are often negligible.

2.3.1.2 Rotations

A rotation is a displacement of every point **r** of a space by the same angle around a central axis. In a three-dimensional vector space defined by a Cartesian system in the coordinates *x*, *y*, and *z*, a rotation by an angle φ around the *z*-axis is described by the matrix

$$\hat{R}^{z}(\varphi) = \begin{pmatrix} \cos\varphi & \sin\varphi & 0\\ -\sin\varphi & \cos\varphi & 0\\ 0 & 0 & 1 \end{pmatrix},$$
(2.4)

from which the form of the unitary matrix \hat{R} for a rotation around an arbitrary axis follows from coordinate transformation. Out of the infinite set of continuous symmetry operations in SO(3), which describes the rotational symmetry of the vacuum, only rotations by integer multiples of 360°, 180°, 120°, 90°, and 60°, associated with the order numbers 1, 2, 3, 4, and 6, respectively, remain as possible symmetry operations of the infinitely extended crystal lattice. The transformation of a physical property $\hat{\chi} = (\chi_{ijk...})$ like the piezoelectric effect $\hat{d} = (d_{ijk})$ discussed in Section 2.1 under an arbitrary three-dimensional rotations $\hat{R} = (R_{il'})$ is given by

$$\chi'_{ijk...n} = R_{ii'}R_{jj'}R_{kk'}\dots R_{nn'}\chi_{i'j'k'\dots n'}.$$
(2.5)

Note that we have $\hat{\chi}' = \hat{\chi}$ if \hat{R} is a symmetry operation.

2.3.1.3 Spatial Inversion

Translations and rotations as continuous geometric transformations are complemented by discrete operations, such as spatial inversion, time reversal, and the already omitted charge reversal. Since these have only two possible eigenvalues, +1 and -1, they are also called parity operations. If we ignore the magnetic structure, we consider only spatial inversion, which mirrors every point **r** of a space at the origin. In three-dimensional vector space, this is described by the anti-unitary matrix \hat{I} with

$$\hat{I} = \begin{pmatrix} -1 & 0 & 0\\ 0 & -1 & 0\\ 0 & 0 & -1 \end{pmatrix}.$$
(2.6)

We can combine pure rotations as in Eq. (2.5) with the spatial inversion operation. For this purpose, the property tensor is expanded into the two eigenstates of the inversion operator associated with the eigenvalues +1 and -1. This leads to an *axial* and a *polar* component with symmetric and antisymmetric transformations, respectively, under the inversion operation. The transformation of the axial and the polar components of the property tensor $\hat{\chi}$ of rank *N* is then given by

$$\begin{aligned} \chi'_{ijk...n} &= +I_{ii'}I_{jj'}I_{kk'} \dots I_{nn'}\chi_{i'j'k'...n'} = +(-1)^N \chi_{i'j'k'...n'} \quad \text{(polar)}, \\ \chi'_{ijk...n} &= -I_{ii'}I_{jj'}I_{kk'} \dots I_{nn'}\chi_{i'j'k'...n'} = -(-1)^N \chi_{i'j'k'...n'} \quad \text{(axial)}. \end{aligned}$$

Therefore, polar tensors of odd rank and axial tensors of even rank change their sign under the inversion operation, whereas axial tensors of odd rank and polar tensors of even rank do not. Because of the dependence of the sign change on the rank of the property tensor, it is useful to introduce *even* and *odd* as additional quasi-parity characterising the rank of the tensor.

2.3.1.4 Time Reversal

For describing the symmetry of magnetically ordered crystals, spatial transformations are no longer sufficient. An intuitive reason for the involvement of the timereversal operation is the classical association of the magnetic moment or spin with a circular electric current, as sketched in Figure 2.2. Inverting the flow of time reverses the direction of this current and therefore breaks the time-reversal symmetry. The association of time reversal to magnetisation reversal is formalised in the field of quantum mechanics, where we introduce the time-reversal operator \hat{T} . In the non-relativistic limit for a spin- $\frac{1}{2}$ particle, it has the form

$$\hat{T} = \begin{pmatrix} 0 & +1 \\ -1 & 0 \end{pmatrix} \widehat{c.c.}$$
(2.8)

The matrix acts on the spinor of the particle, and the operator $\hat{c.c.}$ complexconjugates the spatial part of the wave function. Here, \hat{T} is an antilinear, antiunitary operator. The exchange of the spinor components under \hat{T} represents the reversal of the spin direction and thus relates time reversal to spin reversal or magnetisation reversal in condensed-matter systems. In analogy to spatial inversion, time reversal is a discrete operation with two eigenstates and the two eigenvalues +1 and -1.

Expanding the property tensor into these two eigenstates yields an *i-type* and a *c-type* component with symmetric and antisymmetric transformations, respectively, under time reversal. In three-dimensional space, the transformation properties of the i-type and c-type components of the property tensor under the time-reversal operation are given by

$$\chi'_{ijk\dots n} = +\chi_{i'j'k'\dots n'} \quad \text{(i-type)},$$

$$\chi'_{ijk\dots n} = -\chi_{i'j'k'\dots n'} \quad \text{(c-type)}.$$
(2.9)

Figure 2.2 Association of time reversal with magnetisation reversal. Sketched for the classical interpretation of (a) the spin and (b) the orbital magnetic moment.



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Thus, i-tensors of any rank change their sign under the time-reversal operation, and c-tensors do not. Note that despite their magnetic origin, a process coupling to an even power of the magnetisation is parameterised by an i-tensor because of the even number of factors -1 that time reversal enters into the property tensor.

2.3.2 Combinations of Operations

The transformations introduced in Sections 2.3.1.1–2.3.1.4 can be combined into new types of operations. A rotation combined with a translation is denominated as improper rotation, and the defining axis is a screw axis. A rotation by 180° combined with the inversion operation yields a mirror operation defined by a mirror plane perpendicular to the rotation axis. A mirror operation combined with a translation leads to a glide defined by a glide plane. Combinations of spatial symmetry operations with time reversal are usually indicated by the prefix 'time-odd' or 'c-type', in distinction to 'time-even' or 'i-type' if time reversal is not involved.

2.3.3 Nomenclature

After introducing the different types of symmetry operations that have to be considered in crystals, we now require a nomenclature denoting the operations and their orientation in three-dimensional space. Here, we mostly follow the intuitive nomenclature of Ref. [17], which is summarised in Table 2.1. Only designations necessary for the unambiguous definition of a symmetry operation are usually given.

Table 2.1 Denomination of point-group symmetry operations.

Basic structure of symmetry operation: $N(\pm n_i)[\tau_x, \tau_y, \tau_z]$					
n	Rotation of order <i>n</i> with $n \in \{1, 2, 3, 4, 6\}$				
i	Direction of rotation axis with $i \in \{x, y, z, xy, -xy, \bot\}$				
±	Mathematical sense of rotation				
\overline{n}	Combination of n with spatial inversion operation				
т	Mirror operation as alternative to $\overline{2}$				
n'	Combination of <i>n</i> with time-reversal operation				
N()	Number N of equivalent symmetry operations of this type				
$[\tau_x, \tau_y, \tau_z]$	Translation by vector $\boldsymbol{\tau} = (\tau_x, \tau_y, \tau_z)$				

Only designations necessary for the unambiguous definition of a symmetry operation are usually given. The *z*-axis is chosen as the axis of the highest rotational symmetry. Indices xy and -xy denote the diagonal directions between the x and y axes. The symbol ⊥ denotes the axes perpendicular to the axis of the highest symmetry. Note that the mirror operation m is introduced as an alternative to $\overline{2}$. Furthermore, 1' instead of 1 denotes time reversal in contrast to Ref. [17] in order to adhere to the nomenclature used in the International Tables for Crystallography [15].

For example, a rotation by 180° around the *z*-axis is represented by 2_z instead of $1(+2_z)[0, 0, 0]$. For some symmetries it may be necessary to state the exact orientation perpendicular to the axis of the highest symmetry, *z*. This is expressed by the indices *x*, *y*, *xy*, and -xy, where the latter two refer to the diagonal directions between *x* and *y*. For other symmetries, a general reference to the perpendicular orientation (\bot) may suffice. Furthermore, the rotational symmetry of the *z*-axis defines the number *N* of equivalent symmetry operations perpendicular to it, which is written as N(...).

2.4 Point Groups and Space Groups

In Section 2.3.2, we pointed out that combinations of spatial transformations can reveal new types of operations. Note that if the combination of two transformations is a crystallographic symmetry operation, this does not have to be the case for the constituting operations. The reverse, however, is always true. If two transformations are symmetry operations, their combination is a symmetry operation as well. This has the consequence that the complete set of symmetry operations describing a crystal forms a mathematical group as introduced in Section 2.2, the so-called symmetry group of the crystal. The number of symmetry groups describing all the crystallographic structures that may occur in nature is finite and depends on the type of symmetry operations we include in our consideration. We distinguish between point groups, which involve only operations leaving at least one point in space unchanged, and space groups otherwise. Simply put, point groups can include any type of operation except translations, and space groups include translations as well. The former may be convenient to derive certain physical properties, but only the latter fully describe the structure of a crystal. In Section 2.3.1.1, we argued that for the description of optical processes in the visible range it is often sufficient to work with point-group symmetries. The concepts of point- and space-group symmetries are compared in Figure 2.3.

2.4.1 Point Groups

2.4.1.1 Enantiomorphic Groups

When absorption is negligible, and the Friedel law stating that X-ray diffraction intensity patterns are symmetric with respect to the application of the inversion operation [18] applies, it is impossible to distinguish by diffraction between a centrosymmetric point group and its highest-symmetry non-centrosymmetric subgroups. In that case, the inversion operation can be disregarded in a symmetry analysis. The one-, two-, three-, four-, and sixfold rotations can be combined into 11 so-called *enantiomorphic groups* which are associated with point groups \mathcal{E} containing rotations as the only type of symmetry operation. There are more than five of these because multiple rotations around different axes in three-dimensional space contribute to their formation.



Figure 2.3 Point-group symmetry and space-group symmetry. Exemplified on the unit cell of a tetragonal crystal with atoms as black spheres and *z*-axis values given in units of the lattice constant *c*. (a) Crystal where a rotation by 90° around the *z*-axis is a symmetry operation. The rotation leaves all the points on the central axis unchanged, and the crystal can be described in the frame of point-group symmetries. (b) Crystal where a rotation by 90° around the *z*-axis is a symmetry operation. Because of this displacement, no points are left invariant by this screw operation. The crystal is associated with one of the space-group symmetries. (c) A specific situation may permit the description of a crystal in terms of point-group symmetries in (a) and (b) is addressed by an experiment, the [0, 0, 1/4] displacement associated with the structure in (b) becomes invisible, and the structures in (a) and (b) are both fully captured by the point-group symmetry. Likewise, in optical experiments, displacements are almost imperceptible to visible light with its wavelength of 10³ unit cells so that a description in terms of point-group symmetries suffices.

2.4.1.2 Crystallographic Point Groups

Expanding \mathcal{E} by the inversion operation yields the 32 *crystallographic point groups* \mathcal{G} [12, 17]. These include pure rotations (proper) and rotations combined with the inversion operation (improper). This leads to three types of point groups.

- 11 groups of the type $\mathscr{G} = \mathscr{C} + \hat{I}\mathscr{C}$. In centrosymmetric crystals, every element in \mathscr{E} can be combined with \hat{I} to yield another symmetry operation. The resulting point group thus contains twice as many elements as the corresponding enantiomorphic group.
- 11 groups of the type 𝔅 = 𝔅. In these point groups, Î is not a symmetry operation in combination with any of the elements in 𝔅. Inversion symmetry is broken in every respect, so that 𝔅 contains the same elements as 𝔅.

• 10 groups of the type $\mathscr{G} = \mathscr{C}_{1/2} + \hat{I}(\mathscr{C} \setminus \mathscr{C}_{1/2})$. In these point groups, half of the elements of \mathscr{E} remain symmetry operations, while for the other half the elements are symmetry operations only in combination with \hat{I} .

Note that although the enantiomorphic point group \mathcal{E} and the crystallographic point group $\mathcal{G} = \mathcal{E}$ contain the same set of symmetry operations, they represent different symmetries and point groups. For \mathcal{E} , the inversion operation is absent because it is not considered in the first place (even though it may be a symmetry operation), whereas in \mathcal{G} , the inversion operation is considered and explicitly broken in combination with every element of \mathcal{E} . Thus, \mathcal{E} and $\mathcal{G} = \mathcal{E}$ contain the same set of operations but in different mathematical spaces that, respectively, exclude or include inversion as one of its dimensions.

2.4.1.3 Magnetic Point Groups

Expanding *G* by the time-reversal operation yields the 122 *magnetic point groups* \mathcal{M} , also called *colour groups* or *Shubnikov groups* [11, 17, 19]. As in the case of including the inversion operation, transformations may be symmetry operations as such or in combination with time reversal, or both. This leads to three types of magnetic point groups.

- 32 grey groups with $\mathcal{M} = \mathcal{G} + \hat{T}\mathcal{G}$. In time-reversal-symmetric crystals, every element in \mathcal{G} can be combined with \hat{T} to yield another symmetry operation. The resulting point group contains twice as many elements as the corresponding crystallographic point group. The grey groups describe dia- and paramagnetic crystals and antiferromagnetically ordered crystals in which time-reversal symmetry is broken only in combination with a translation.
- 32 colourless groups with $\mathcal{M} = \mathcal{G}$. In these point groups, \hat{T} is not a symmetry operation in combination with any of the elements in \mathcal{G} , and \mathcal{M} contains the same elements as \mathcal{G} . Colourless groups describe crystals with certain types of long-range magnetic order.
- 58 black-and-white groups with $\mathcal{M} = \mathcal{G}_{1/2} + \hat{T}(\mathcal{G} \setminus \mathcal{G}_{1/2})$. In these point groups, half of the elements of \mathcal{G} remain symmetry operations, while for the other half, the elements are symmetry operations only in combination with \hat{T} . Black-and-white groups also describe crystals with certain types of long-range magnetic order.

In analogy to the discussion on \hat{I} , we have to distinguish the colourless magnetic point groups from the crystallographic point groups with the same set of symmetry operations. Both groups represent different symmetries and point groups because they are defined in different mathematical spaces. Usually they are both represented by the same symbol so that it needs to be clarified whether a discussion refers to crystallographic or magnetic symmetries. When addressing magnetic symmetries, the grey groups are distinguished from the colourless groups by adding 1' to the symbol of the former. The addition indicates that time reversal is a symmetry operation in combination with all elements of the associated crystallographic group.

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For example, the crystallographic point-group symmetry $2 = \{1, 2_z\}$ is associated with the grey magnetic point-group symmetry $21' = \{1, 2_z, 1', 2'_z\}$ and the colourless magnetic point-group symmetry $2 = \{1, 2_z\}$. We will always make clear through context or explicit reference whether we refer to crystallographic or magnetic point groups in a discussion.

2.4.1.4 Other Types of Point-Group Symmetries

The same procedure used for the implementation of spatial and temporal inversion symmetries can be applied to include further types of parity operations. For example, the sense of the rotation of a subset of atoms within a unit cell was proposed to define a distortive parity operation denominated as 'roto-inversion', \hat{S} [20]. With 'counter-clockwise' (+1) and 'clockwise' (-1), we obtain its two eigenstates and eigenvalues. In the specific example in Ref. [20], crystals without magnetic order were considered so that in the description of roto-symmetries, \hat{I} and \hat{S} replace \hat{I} and \hat{T} . We thus obtain the same colour groups as for magnetically ordered crystals, albeit with the substitution of magnetic order by distortive order. It is still debated if three-dimensional space permits such additional parity operations, or if these are only replica of the existing symmetry operations in space and time.

Quasicrystals are structures that are ordered but not periodic in threedimensional space [21]. They exhibit symmetries under certain point-group operations but no translational symmetries and in particular no unit cell. The point operations include rotational axes of an order *n* not permitted in crystals, such as n = 5, 10, or 12.

Furthermore, crystals may exhibit incommensurate forms of ordering, that is a periodicity in the arrangement of atoms, electrons, or spins that cannot be written as a rational multiple of the lattice constants [21]. As in the case of quasicrystals, these structures exhibit symmetries under certain point-group operations but no lattice-translational symmetries. They can, however, be described by referring to the same crystallographic or magnetic point-group symmetries as in the case of conventional (commensurate) crystals. Alternatively, incommensurate crystals as well as quasicrystals may be described as regular lattice-periodic structures in spaces of more than three dimensions. It is the projection onto three-dimensional, real space that destroys their translational symmetries.

2.4.2 Space Groups

In certain cases, omission of translational symmetry operations in optics is no longer a good approximation. This may be the case if spectral features in the optical response that originate in the exact position of the atoms in the unit cell become important, or if the translational symmetry operations introduce a distinction between crystallographic directions that point operations would not provide. By including translations as symmetry operations, we expand the number of crystallographic symmetry groups to 230 and the number of magnetic symmetry groups to 1651. For the definitions and characteristics of all these groups, the International Tables for Crystallography [15], the Bilbao Crystallographic Server [22], and the magnetic group tables by Litvin [23] are helpful sources.

2.5 From Symmetries to Properties

2.5.1 Deriving the Components of the Property Tensors

Equation (2.5) describes how a tensor $\hat{\chi}$ parameterising the macroscopic physical properties of a material is transformed into the tensor $\hat{\chi}'$ under the application of a rotation or of spatial or temporal inversion. If such a transformation is a symmetry operation, we have $\hat{\chi}' = \hat{\chi}$, and relations as in Eq. (2.5) become a system of linear equations that allows to derive conclusions about the components of $\hat{\chi}$ and, hence, on the manifestation of the physical effect represented by this tensor. Typical conclusions are that a certain tensor component vanishes or stands in a linear relation to other tensor components. Let us, as an example, consider the dielectric tensor $\hat{\epsilon}$ mediating the relation between an applied electric field **E** and the resulting dielectric shift **D** in a material according to $D_i = \epsilon_0 \epsilon_{ij} E_j$ with ϵ_0 as the vacuum permittivity. In a material possessing a threefold symmetry axis along *z*, we get

$$\epsilon_{ij} = R^{z} (120^{\circ})_{ii'} R^{z} (120^{\circ})_{jj'} \epsilon_{i'j'}, \qquad (2.10)$$

with \hat{R}^z as in Eq. (2.4) for $\varphi = 120^\circ$. This leads to the two equations

$$\epsilon_{31} = -\frac{1}{2}\epsilon_{31} + \frac{\sqrt{3}}{2}\epsilon_{32},\tag{2.11}$$

$$\epsilon_{32} = -\frac{\sqrt{3}}{2}\epsilon_{31} - \frac{1}{2}\epsilon_{32},\tag{2.12}$$

and thus to the solution

$$\epsilon_{31} = \epsilon_{32} = 0. \tag{2.13}$$

Proceeding in this fashion, one can determine the zeroness or interrelation of all the components of \hat{e} . The transformation behaviour under spatial inversion or time reversal allows to specify the form of the property tensors $\hat{\chi}$ further. Applying this procedure to all the 122 point groups describing crystals with and without magnetic order results in not more than 21 types of tensors at any rank considered. The vanishing components and the interrelation of the non-zero components for the 21 types of tensors are tabulated up to rank four [17], and for even higher ranks other sources can be consulted [24].

2.5.2 Parity of the Property Tensors

The relations imposed by the parity operations are especially stringent. For example, all axial i-tensors of even rank and all polar i-tensors of odd rank vanish in centrosymmetric crystals because for these, Eq. (2.7) leads to $\hat{\chi} = -\hat{\chi} \equiv 0$. Table 2.2 lists further tensors vanishing if certain parity operations are symmetry operations.

Furthermore, the parity of the property tensors can be concluded from the parity of the measurable physical quantities (called *observables*) they connect. Let us, for

					i-ter	isors		c-tensors				
Symmetry element		Number of groups	Even rank		Odd rank		Even rank		Odd rank			
			Polar	Axial	Polar	Axial	Polar	Axial	Polar	Axial		
Î	Î	<i>Î</i> Î	11	1	0	0	1	0	0	0	0	
_	Î	_	21	1	1	1	1	0	0	0	0	
Î	—	—	21	1	0	0	1	1	0	0	1	
—	_	$\hat{T}\hat{I}$	21	1	0	0	1	0	1	1	0	
—	—	—	48	1	1	1	1	1	1	1	1	

Table 2.2 vanishing tensors in the 122 colour point group	Table 2.2	Vanishing	tensors in	the 122	colour	point grou	ips
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Zeroes and ticks denote vanishing and non-vanishing tensors, respectively. The upper two lines refer to the grey groups describing systems with or without magnetic order. The lower three lines refer to the 90 colourless and black-and-white groups exclusively describing magnetically ordered materials.

example consider the (converse) piezoelectric effect of Eq. (2.1). Strain is represented by a polar even-rank i-tensor, and for the electric field it is a polar odd-rank i-tensor. Then, the property tensor for the piezoelectric effect has to be a polar odd-rank i-tensor in order to establish the same set of parities on both sides of the equation. For property tensors of any other parity, application of the associated parity operation would lead to $\hat{a}^{pe} = -\hat{a}^{pe} \equiv 0$. Let us now look at the (converse) piezomagnetic effect, where a magnetic field **H** rather than an electric field **E** induces strain:

$$S_{ij} = d_{ijk}^{pm} \quad H_k$$

$$| \quad | \quad | \quad .$$

p, e, i a, o, c a, o, c (2.14)

The letters representing the parities immediately reveal that the piezomagnetic effect, represented by \hat{a}^{pm} , is parameterised by an axial odd-rank c-tensor. Therefore, it can occur in magnetically ordered materials only.

2.5.3 Introducing Inhomogeneity

So far, we only considered static physical effects that are homogeneously present in infinitely extended crystals. Once we introduce spatial dependence, we have to take into account that the transformations introduced in Section 2.3.1 do not only act on the physical property considered but also on the point in space and time to which this property is assigned. With *A* as property, \hat{O} as transformation, and **r** and *t* as spatial and temporal coordinates, we get

$$\hat{O}[A(\mathbf{r},t)] = [\hat{O}A]([\hat{O}\mathbf{r}],[\hat{O}t]).$$
(2.15)

For instance, the magnetic and electric field are prototypical examples associated with axial and polar vectors, respectively. In Figure 2.4a, **H** keeps its sign under



Figure 2.4 Field distributions and the inversion operation. (a) Homogeneous vector field. The inversion operation applied with respect to the point '×' retains and reverses sign in the case of a magnetic and an electric field, respectively. (b) Inhomogeneous vector field. Behaviour under the inversion operation is opposite to (a) because both the field and its distribution change sign under the inversion.

the inversion operation, and for **E** it changes. With the field distributions shown in Figure 2.4b, however, $\mathbf{H}(\mathbf{r})$ changes its sign under \hat{l} , and $\mathbf{E}(\mathbf{r})$ does not. Nevertheless, they remain to be axial and polar vectors, respectively, because the reversed behaviour is caused by the spatial distribution of the fields and not by the fields as such.

Temporal inhomogeneity is introduced once we consider optical effects because these involve time-dependent electric and magnetic fields proportional to $e^{i\omega t}$, with ω as frequency [25]. The consequence of the periodic time dependence is nicely illustrated by the Faraday effect, which describes the rotation of the plane of polarisation ($\sim \mathbf{P}(\omega)$) of a light wave $\mathbf{E}(\omega)$ passing through a transparent material exposed to a static longitudinal magnetic field $\mathbf{H}(0)$. Applying the same analysis as in Eq. (2.14) leads to

$$P_{i}(\omega) = F_{ijk} \quad H_{j}(0) \quad E_{k}(\omega)$$

$$| \qquad | \qquad | \qquad | \qquad | \qquad , \qquad (2.16)$$
p, o, i
$$a, o, c \quad a, o, c \quad p, o, i \quad \rightarrow \text{ wrong!}$$

with the conclusion that the Faraday effect is parameterised by the axial odd-rank c-tensor \hat{F} . This may appear as correct at first glance because the Faraday effect is the prototypical time-reversal-symmetry-breaking magneto-optical effect. Its occurrence is not limited to magnetically ordered materials, however, as the parity analysis in Eq. (2.16) would imply. Therefore, the analysis cannot be correct.

The apparent contradiction is resolved by including the periodic time dependence of the electric field representing the light wave. We have

$$\mathbf{E}(\omega) = \mathbf{E}_0 \mathrm{e}^{\mathrm{i}\omega t},\tag{2.17}$$

the time reversal of which converts this into

$$\hat{T}\mathbf{E}(\omega) = \mathbf{E}_0 e^{i\omega(-t)} = \mathbf{E}^*(\omega)t, \qquad (2.18)$$