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A Preview of the Subject of the Book

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

HÉLOÏSE: 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.

Nonlinear Optics on Ferroic Materials, First Edition. Manfred Fiebig.

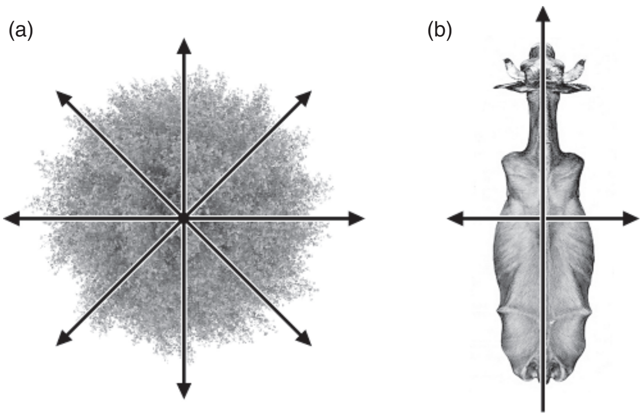

Figure 1.1 The potential of symmetry analysis. (a) Deciduous tree from above. There is no direction here that stands out above another, see the double arrows. In consequence, rotation around the centre does not change the general appearance of the tree. With the lack of a built-in direction it is expected 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

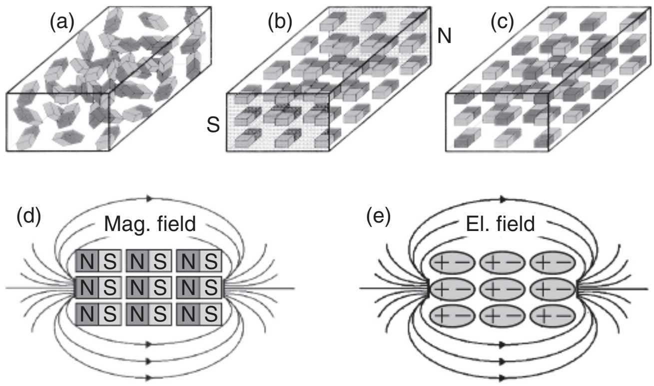

Figure 1.2 Magnetic and electric order of materials. (a) Atoms in a crystal representing minuscule magnets. In most materials these so-called magnetic moments point in random directions so that the total magnetic fields cancel out. (b) Spontaneous order may occur, where all the atomic magnets point in 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 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.

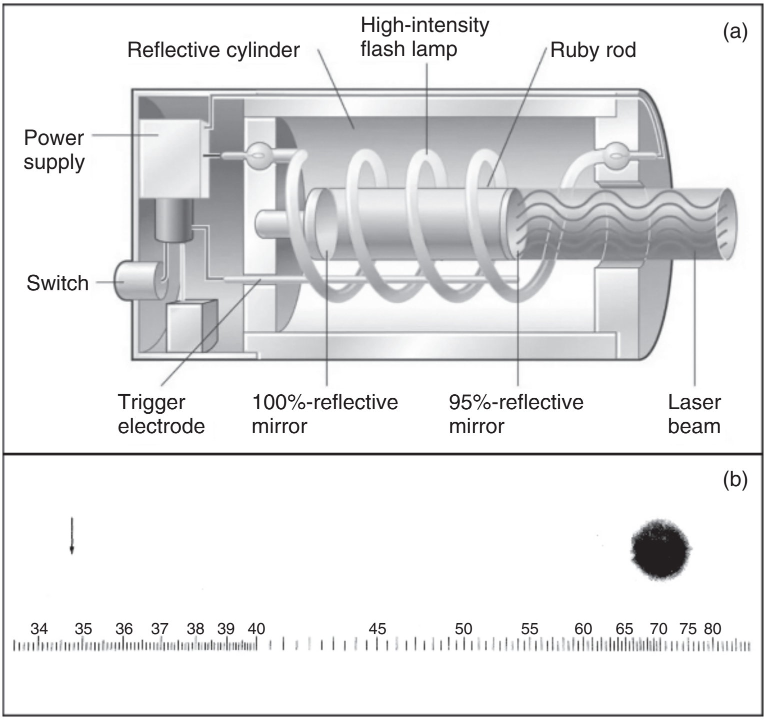

Figure 1.3 Nonlinear optical processes with lasers. (a) Design of the ruby laser used for the first demonstration of laser emission in 1960 [3]. A ruby crystal is optically excited with light from a flash lamp and driven to emit directed visible and very 'clean' deep red light with the help of two parallel 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.

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 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.