Coupled electricity and magnetism in solids:
multiferroics and beyond

D. I. Khomskii

II. Physikalisches Institut, Universität zu Köln,
Zülpicher Str. 77, 50937 Köln, Germany

Abstract
The interplay of electricity and magnetism, one of the cornerstones
of modern physics, takes a special form in solids in such phenomena
as magnetoelectricity and the possibility of multiferroic behaviour. In
this paper I give a short survey of the main notions of this field, paying
special attention to microscopic aspects. Some related phenomena,
such as electric activity of magnetic domain walls, etc., are also shortly
discussed.

1 Introduction
The intrinsic coupling of electricity and magnetism is one of the cornerstones
of modern physics. It goes back to the famous Maxwell equations, or even
erlier, to Michael Faraday, and one can find even earlier reports pointing in
that direction. This coupling plays crucial role in all modern physics, and
it is one of the foundations of modern technology — e.g. in the generation
of electricity in electric power stations, electric transformers, etc. Recently
this field acquired new life in spintronics, the idea of which is to use not
only charge, but also spin of electrons for electronic applications. Mostly
one deals in this field with the influence of magnetic field and/or magnetic
ordering on transport properties of materials — for example the well-known
magnetoresistance or the work of magnetic tunnel junctions. But very in-
teresting such effects can also exist in insulators. These are for example the
(linear) magnetoelectric (ME) effect, or the coexistence and mutual influence
of two types of ordering, magnetic and ferroelectric (FE) ordering in \textit{multi-ferroics} (MF). Such phenomena are very interesting physically, and are very promising for practical applications, e.g. for addressing magnetic memory electrically without the use of currents, or as very efficient magnetic sensors. These factors probably caused such a significant interest in this field. It is now one of the hottest topics in condensed matter physics, and, besides magnetoelectrics and multiferroics per se, the study of these has many spin-offs in the related fields of physics, such as the study of magnetoelectric effects in different magnetic textures (domain walls, magnetic vortices, skyrmions etc.)

There are already several good reviews of this field \[1, 2, 3, 4, 5, 6, 7\], and there exists a very complete and useful collection of short reviews on multiferroics in the special issue of Journal of Physics of Condensed Matter \[8\]. There is also a chapter on multiferroics in my recent book \[9\]. In the present text, which is written as an introductory chapter for a planned book on multiferroics, I will more or less follow the general outline of my short review on “Multiferroics for pedestrians”, published in Physics: Trends \[7\] — of course with significant additions.

Multiferroics are materials with coexisting magnetic and ferroelectric ordering. These systems are extremely interesting physically, and they promise many important practical applications. However one has to realize that for many practical applications, such as attempts to write and read magnetic memory in hard discs electrically, using electric fields rather than currents (e.g. with gate voltage devices), one needs not so much multiferroics but rather materials with good magnetoelectric properties: one must be able to \textit{modify} the magnetic state by a changing electric field. But the idea is that it is precisely multiferroic materials in which the change of magnetic state by electric field, or vice versa, may be especially strong. From this point of view, various textures in magnetic materials which can have magnetoelectric response — such as certain domain walls of skyrmions — also attract now considerable attention. These topics will be also mentioned below.

2 Some historical notes

When one describes the field of magnetoelectrics and multiferroics, the first reference one usually gives is that to Pierre Curie \[10\], who shortly noticed the possibility of having both magnetic and electric orderings in one material.
But the real story began with a short remark in one of the famous books on theoretical physics by Landau and Lifshitz [11], who wrote in 1959:

“Let us point out two more phenomena, which, in principle, could exist. One is piezomagnetism, which consists of linear coupling between a magnetic field in a solid and a deformation (analogous to piezoelectricity). The other is a linear coupling between magnetic and electric fields in a media, which would cause, for example, a magnetization proportional to an electric field. Both these phenomena could exist for certain classes of magnetocrystalline symmetry. We will not however discuss these phenomena in more detail because it seems that till present, presumably, they have not been observed in any substance.”

Indeed, at the moment of publication of that volume there were no known real examples of magnetoelectric or multiferroic systems. But already less than a year after its publication the seminal paper by Dzyaloshinskii appeared [12], who on symmetry grounds predicted that the well-known antiferromagnet Cr$_2$O$_3$ should exhibit the linear ME effect. And next year this effect was indeed observed in Cr$_2$O$_3$ by Astrov [13]. After that a rapid development of this field followed, initially in the study of magnetoelectrics, see e.g. [14]. But very soon the ideas of not only the ME effect, but of real multiferroics were put forth. Soon the first multiferroic — a material in which (anti-)ferroelectric and ferroelectric ordering are present simultaneously — was discovered by Ascher, Schmid et al. [15] – the Ni–I boracite. (It was in fact Hans Schmid who later coined the very term “multiferroics” in connection with such materials [16]). An active program to synthesize such materials artificially was initiated, predominantly by two groups in the former Soviet Union: in the group of Smolenskii in Leningrad (present-day St. Petersburg) and in the group of Venevtsev in Moscow.

However, after considerable activity in the 1960s and 1970s, the interest in this field faded somewhat. A new surge of activity appeared at around 2000, and there were three factors which stimulated it:

The first was the realization of an interesting and challenging problem in the physics of magnetic and ferroelectric materials, mostly on the example of perovskites. There are quite a lot of magnetic perovskites, including famous colossal magnetoresistance manganites, or the “two-dimensional perovskite” La$_2$CuO$_4$ — the parent material of High-Temperature superconducting cuprates. Extensive discussion of these materials, with many tables,
is contained in the collection compiled by Goodenough and Longo in the Landolt-Börnstein Encyclopaedia of Physics [17]. Another, even more extensive collection of tables of ferroelectric perovskites, starting with the equally famous material BaTiO$_3$, was published by a group of Japanese scientists [18]. And, surprisingly enough, a comparison of these extensive collections of tables, 100–300 pages each, demonstrates that there is practically no overlap between them: a perovskite is either magnetic or ferroelectric, but practically never both simultaneously (of course it may be neither, as is the case with the prototype mineral perovskite CaTiO$_3$, which gave the name to this whole family). What is the reason for this mutual exclusion, and can one go around it? This problem was known already in 1970–1980s, but was actually formulated only in 1999 during a workshop in Santa Barbara, and publicised after 2000 [19, 20], and it attracted the attention of scientific community. This problem will be discussed below, in Sec. 6.

But of course the most important were two experimental breakthroughs. One was the fabrication and study of very good films of, it seems, the best multiferroic material known at present, BiFeO$_3$, by Ramesh and his group [21]. This gave a possibility of studying the MF effects, and immediately opened perspectives of very appealing practical applications. BiFeO$_3$ remains until today the favourite material for many investigations, both in basic research and in applied fields.

The second achievement was the discovery by two groups, of Kimura and Tokura, and of Sang-Wook Cheong, of a novel class of multiferroics [22, 23]. In multiferroics that were known previously the ferroelectric and magnetic orderings occurred independently and were driven by different mechanisms; typically, although not always, FE ordering starts at higher temperature. In the novel class of multiferroics discovered in [22, 23], FE is driven by a particular type of magnetic ordering, and occurs only in the magnetically-ordered phase. One can call the first group “type-I multiferroics”, and the second group “type-II multiferroics” [7]. I will discuss this classification and the microscopic mechanisms in action in each of these classes in Sec. 5. Here I only want to stress that these two experimental breakthroughs gave new life to the whole field of MF and led to an enormous increase of activity in this field.
3 Magnetoelectric effect; symmetry considerations

The specific feature of magnetoelectric materials is the possibility of generating electric polarization by magnetic field, and vice versa, magnetization by electric field. This can be described by the relations

\[ P_i = \alpha_{ij} H_j + \beta_{ijk} H_j H_k + \cdots, \]  
\[ M_j = \alpha_{ji} E_i + \beta_{jik} E_i E_k + \cdots, \]

where we use the standard convention of summation over the repeated indices. Terms quadratic in \( E, H \) are typically more common and less interesting; the most interesting effect is the presence of the first, linear terms above. This is referred to as the linear ME effect, or simply the ME effect.

One can also describe the linear ME effect by including in the expression for the free energy the term

\[ F_{\text{ME}} = -\alpha_{ij} E_i H_j. \]

As the polarization and the magnetization are given by \( P = -\partial F/\partial E \) and \( M = -\partial F/\partial H \), one immediately obtains from this expression for the free energy the first terms in (1) and (2).

As we see, in general in a crystal the magnetoelectric coefficient \( \alpha \) is a tensor. It can have symmetric and antisymmetric components. The symmetric part of this tensor can always be transformed to a diagonal form

\[ \alpha_{ij} = \alpha_i \delta_{ij} \]  

(where \( \delta_{ij} \) is the Kronecker symbol). In this case the polarization for the magnetic field along the main axes would be parallel to the magnetic field. But there can also be an antisymmetric part of the magnetoelectric tensor. It is known that such an antisymmetric tensor, with independent components \( \alpha_{12}, \alpha_{13} \) and \( \alpha_{23} \), is equivalent to an axial vector, or pseudovector

\[ T_i = \varepsilon_{ijk} \alpha_{jk} \]

where \( \varepsilon_{ijk} \) is the totally antisymmetric Levi-Civita symbol. This pseudovector \( T \) is called the toroidal moment. If the system has a nonzero toroidal
moment, then, from (1), (2), (5) one can see that for example the polarization
in an external magnetic field would be

$$P \sim T \times H,$$

(6)

and magnetization would be

$$M \sim T \times E,$$

(7)
i.e. they would be perpendicular to the external fields.

A very important role in the ME effect is played by symmetry consider-
ations. First of all, these refer to the symmetry with respect to spatial
inversion, $J$, and time reversal, $T$. Electric field, polarization and electric
dipole moments are usual vectors, changing sign under spatial inversion, but
remaining the same under time reversal:

$$J_P = -P, \quad J_E = -E,$$

$$T_P = P, \quad T_E = E.$$

(8)

On the other hand, magnetization, and the magnetic field itself, are axial
vectors, or pseudovectors, odd with respect to time reversal, but even with
respect to spatial inversion,

$$J_M = M, \quad J_H = H,$$

$$T_M = -M, \quad T_H = -H.$$

(9)

One can easily understand these rules when one recalls that magnetic field
and magnetic moments are created by currents $J = ev = e \, dr/dt$; for exam-
ple, for circular currents shown in Fig. 1 we have $M \sim r \times J$. One sees from
this expression that $M$ is even for spatial inversion ($r \to -r$), but odd for
time reversal ($t \to -t$).

![Fig. 1](image_url)

Using this picture, one can also obtain the transformation rules of e.g.
$M$ or $P$ under mirror reflections, illustrated in Fig. 2 (see also [9]): under
mirror reflections the components of $\mathbf{P}$ and $\mathbf{M}$ parallel and perpendicular to the mirror plane change as

$$
P_{\perp} \rightarrow -P_{\perp}, \quad P_{\parallel} \rightarrow P_{\parallel},$$

$$
M_{\perp} \rightarrow M_{\perp}, \quad M_{\parallel} \rightarrow -M_{\parallel}.
$$

(10)

![Diagram of mirror reflections](image)

**Fig. 2**

From the rules (8), (9) one sees that the linear ME effect (liner terms in (1), (2), or (3)) can exist in a system only if both inversion and time reversal are simultaneously broken: the energy (3) should be a scalar, and thus the ME coefficient $\alpha$ should be both $\mathcal{J}$- and $\mathcal{T}$-odd. For that, first of all, the system should have some magnetic ordering which breaks time reversal. In most cases this is the standard magnetic ordering, for which the average spin at a site $\langle S_i \rangle \neq 0$, but one cannot exclude more complicated states such that not the magnetic dipole $\langle S \rangle$ is nonzero, but rather there exists some non-zero higher-order spin correlation function, containing an odd number of spins — e.g. the magnetic octupole $\sim \langle S_1 S_2 S_3 \rangle$. And the spatial inversion should also be broken in order to have the linear ME effect; often this symmetry is broken just by a particular type of magnetic ordering.
In general, the free energy may also contain terms of higher order, not only those presented in eq. (3). For example, we may have terms of the type \( \beta_{ijk} E_i H_j H_k \), or similar terms written as a function of order parameters \( P \) and \( M \), e.g. \( \sim \beta_{ijk} P_i M_j M_k \), or terms \( \sim P^2 M^2 \). The conditions for their appearance are often not so stringent as those for linear ME coupling. We will not, however, consider such terms below, and will concentrate on the linear ME effect.

There is one general relation between the ME response function \( \alpha_{ij} \) and the usual dielectric and magnetic response, characterized by the dielectric constant \( \epsilon_{ij} \) (or the corresponding electric susceptibility, or polarizability), and the magnetic response characterized by magnetic permeability \( \mu \) or magnetic susceptibility \( \chi \), with \( \mu = 1 + 4\pi\chi \). This constrain has the form \[ \alpha^2 < \chi_e \chi_m \] where \( \chi_e \) and \( \chi_m \) are the electric and magnetic susceptibilities. We see that one can hope to obtain strong ME coupling for example close to a ferroelectric or magnetic transition, in which (for II order transitions) \( \chi_e \) or \( \chi_m \) diverge, \( \chi_e \rightarrow \infty \) or \( \chi_m \rightarrow \infty \).

One more point is worth addressing here. We now know very well that the electric and magnetic responses are in general frequency- and momentum-dependent, \( \epsilon(q, \omega) \), \( \chi(q, \omega) \). This dependence has very definite physical meaning. Thus for example the dielectric function contains terms such as

\[ \epsilon(q, \omega) \sim \sum c_i \frac{\omega^2 - \omega_i^2(q)}{\omega^2 - \omega_i^2(q)} \]  

i.e. it has poles at the positions of dipole-active collective excitations \( \omega_i(q) \), for example optical phonons. These modes give definite signatures e.g. in the optical properties of solids. Similarly, the structure of \( \chi(q, \omega) \), which can be measured for example by magnetic neutron scattering, tells us about magnetic excitations in the system, such as spin waves with their spectrum \( \omega(q) \); and the existence of (strong) maximum of \( \chi(q, 0) \) at a certain \( q \)-value \( q_0 \) may be a signature of eventual magnetic instability of the system, such as the formation of spin density wave with momentum \( q_0 \), etc.

One should think that, similarly, the ME response function \( \alpha \) should also have both frequency- and momentum-dependence, \( \alpha(q, \omega) \). This question was not, to the best of my knowledge, yet studied in a general form for ME materials. Apparently the electromagnons [26] are related to this question —
they should be the poles of both $\epsilon$ and $\alpha$, similar to eq. (12). But what could be, for example, the $q$-dependence of $\alpha$, what would be its significance, and how can one measure it, are still open questions. One could think that there should also be some general relations for $\alpha(q, \omega)$ similar to the Kramers-Kronig relations or to the optical sum rule for $\epsilon(q, \omega)$, however I am not aware of any such general treatment yet (possibly one could find some related results in the literature, but they are not formulated in this language).

4 Multiferroics

4.1 General considerations

By multiferroics in a narrow sense we refer to materials having simultaneously both magnetic and ferroelectric ordering, i.e. having two order parameters $M(r)$ and $P(r)$. Magnetic ordering could be of different types: ferromagnetic, ferri- or antiferromagnetic, or it could be of some more complicated type. But for electric ordering one has in mind a real FE ordering, $\langle P \rangle \neq 0$. Sometimes in the field of ferroelectricity one also speaks about antiferroelectrics (AFE), but one has to realize that this notions has no strict physical meaning. Magnetic transitions, of any kind, always correspond to symmetry-breaking: going from paramagnetic to magnetically-ordered state we break at least the time reversal symmetry (and maybe some spatial symmetries as well). Similarly, FE transition corresponds to a change of symmetry in the system from centrosymmetric to noncentrosymmetric one. However, the nominally antiferroelectric transitions do not necessarily break any symmetry: one can always formally consider any system as having electric dipoles, e.g. inside a unit cell, pointing in opposite directions. In this sense any structural transition in a solid is accompanied by some charge redistribution and could be formally called an AFE. Still, sometimes it can make sense to speak about an AFE transition, if this structural transition is accompanied by relatively strong anomalies in the dielectric constant $\epsilon$; but one has to realize that this notion has no rigorous meaning. In any case, in the field of multiferroics we always have in mind the appearance of a real FE polarization, which is nonzero when averaged over the whole sample — although sometimes we also speak about local polarization.

\(^{1}\)Sometimes one includes among multiferroics also systems with a third type of ordering — a ferroelastic one. Here, however, we will not consider it.
The different character of electric and magnetic ordering is reflected in one important aspect. The magnetic order parameter, e.g. the magnetization of a ferromagnet \( \langle M \rangle \) or sublattice magnetization \( L = \langle M_1 - M_2 \rangle \) of an antiferromagnet are well-defined quantities, having absolute meaning. This however is not the case with electric polarization: it may depend for example on the choice of the unit cell, cf. Fig. 3. It looks that with the choice of the unit cell as shown in Fig. 3(a) the polarization points from left to right; however in the same system but with a different choice of the unit cell, Fig. 3(b), it points from right to left. And indeed, the accurate treatment shows, see for example a very pedagogical explanation in [27], that the absolute value of polarization is not a uniquely defined quantity, but the change of polarization with changing external conditions, e.g. temperature or electric field, is. This is also reflected in that fact that one has to use special theoretical methods (the so-called Berry phase methods) for \textit{ab initio} calculation of polarization.

![Fig. 3](image_url)

The very term “multiferroic” was proposed by H. Schmid [16]. In his review article [28] Schmid also presented a classification of different symmetry classes which allow for simultaneous presence of both FE and magnetic ordering.

In speaking about multiferroics, symmetry considerations play a crucial role. Both time reversal \( \mathcal{T} \) and spatial inversion symmetry \( \mathcal{J} \) should be broken. And one also needs one unique vector \( \mathbf{P} \) which has to go to \(-\mathbf{P}\) under inversion. One sees that these symmetry requirements are the same as those needed to get the linear ME effect. An important question is in which cases would one get ME, with polarization existing only in an external (magnetic) field, and when will we have real multiferroics, with spontaneous polarization existing without any external field. For ME both \( \mathcal{T} \) and \( \mathcal{J} \) should be broken, but the product \( \mathcal{T}\mathcal{J} \) is conserved: by consecutive application of time reversal and spatial inversion we would return to the initial state. For multiferroics, however, not only \( \mathcal{T} \) and \( \mathcal{J} \) but also the product \( \mathcal{T}\mathcal{J} \) should be broken. Thus by looking at these symmetries one can understand whether a particular
material with a given magnetic structure would be a real multiferroic or only a magnetoelectric. The examples mentioned above demonstrate this. The classical ME material Cr$_2$O$_3$ has a crystal and magnetic structure with the main element shown in Fig. 4(a) (the inversion centre is marked by the encircled cross $\otimes$). Of course, as in all magnetic states, time-reversal is broken right away. According to the rules formulated above, spatial inversion is also broken (it transforms spin $\uparrow$ to $\downarrow$). But simultaneous inversion and time reversal (inversion of spin directions) returns the state to the original one, i.e. $\mathcal{T}|\text{in}\rangle = -|\text{in}\rangle$, $\mathcal{J}|\text{in}\rangle = -|\text{in}\rangle$, but $\mathcal{T}\mathcal{J}|\text{in}\rangle = |\text{in}\rangle$. Therefore this system is ME but not MF. On the other hand, for example in the structure shown in Fig. 4(b), with alternation of ions with different charges, e.g. $+$ and $-$, and with the magnetic structure $\uparrow\uparrow\downarrow\downarrow$ (this is a schematic representation of a real situation in Ca$_3$CoMnO$_6$ [29], see also [30] and Fig. 10 below), not only $\mathcal{T}$ and $\mathcal{J}$, but also $\mathcal{T}\mathcal{J}$ are broken, time reversal following inversion leading to a state different from the initial one. And indeed this gives real multiferroics [29].

![Fig. 4](image)

One still has to be slightly careful with his classification: to have a real FE in the usual sense one has to have the ability to reverse polarization, $P \rightarrow -P$, by applying a proper electric field $E$ (the poling procedure, which gives the famous polarization loop, $P(E)$ hysteresis). In some systems, however, the electric field required for that is too strong to be realized.
in practice, so that the polarization is always pointing in one direction, and we cannot switch it. In this case one speaks not about ferroelectrics, but rather about pyroelectrics [11]. There are such examples also among “multiferroic” compounds. Thus PbVO$_3$ has a tetragonal structure of the same type as the famous ferroelectric PbTiO$_3$, but the distortion in it leading to the formation of dipole moments is so strong that the polarization cannot be reversed [31, 32] (maybe it would possible to realize this in corresponding films?). Thus PbVO$_3$ should rather be called a magnetic pyroelectric, not a multiferroic. Still, symmetry considerations are extremely useful, and actually crucial in the whole big field of multiferroics. One can find corresponding treatment for example in the review [28] or in [33]. We will not dwell on this topic any more, and will rather discuss more microscopic aspects of the physics of multiferroics.

5 Different types of multiferroics

Speaking of microscopic mechanisms, one can first of all say that, despite the huge variety of different types of magnetic ordering, most of all “strong” magnets are conceptually the same, see e.g. [9]: due to strong electron–electron interaction or strong electron correlations the state is formed with localized electrons (which for integer number of electrons per cite are the Mott, or Mott–Hubbard insulators), i.e. the state with localized magnetic moments — localized spins. The exchange interaction between these localized moments leads to a certain magnetic ordering at low temperatures. Depending on specific details, such as electron configuration of respective ions, orbital occupation, detailed type of the lattice, etc., we can have quite diverse types of magnetic ordering, but the general picture — the presence of localized electrons or localized spins with particular exchange interaction — remains the same.

The situation with ferroelectrics is more diverse and much more complicated. There exist many different microscopic mechanisms leading to ferroelectric behaviour. And all the diversity of ferroelectrics and of eventual multiferroics is mainly connected just with this diversity of mechanisms of ferroelectricity. Thus, we can have systems in which there exist structural units, e.g. molecules similar to HCl, each of which has nonzero dipole moment just “by construction”. And some ordered arrangement of such units could in principle make a material ferroelectric. It is known for example that
among many forms of water ice there is one which is ferroelectric.

Another mechanism is met in hydrogen-bonded ferroelectrics. To these belong some inorganic compounds, e.g. KH$_2$PO$_4$ (KDP), but mostly organic systems, for example the first ferroelectric discovered in nature — the Rochelle or Seignette’s salt NaKC$_4$H$_4$O$_6$ · 4H$_2$O (this compound even gave the name to this very phenomenon in several languages, where ferroelectricity is called seignetoelectricity) — although the exact nature of FE in this material is still a matter of debate. In both cases above there may exist some magnetic ions in “other parts” of the system, so that in effect such systems may become multiferroic.

For us, however, other types of multiferroics are of more importance. These are FE or MF with FE driven by the covalency of transition metal (TM) ions with surrounding cations (ligands), for example with oxygen; “geometric” ferroelectrics; and ferroelectrics with lone pairs. We will now proceed to a short description of these three classes of materials. However, before that, we will briefly discuss two general notions.

One can divide all multiferroics into two big groups, which we can call type-I and type-II multiferroics [7]; we have already shortly mentioned this classification in Sec. 2. The multiferroics we have mostly discussed until now, with the mechanisms of ferroelectric ordering listed above, have independent mechanisms of FE and magnetic ordering, occurring at different temperatures (usually with FE transition above the magnetic one, but not necessarily so). These are type-I multiferroics. Ferroelectricity often occurs in them at rather high temperatures — thus in BiFeO$_3$ $T_{FE}$ $\sim$ 1100 K, and in YMnO$_3$ $T_{FE}$ $\sim$ 1000 K. Magnetic ordering, occurring independently, can also be rather high: in BiFeO$_3$ $T_N$ = 640 K, so that it is a good multiferroic already at room temperature. In general such systems can have quite large spontaneous polarization, which in BiFeO$_3$ reaches 80–100 $\mu$C/cm$^2$ — larger that in BaTiO$_3$ ($\sim$ 60 $\mu$C/cm$^2$). Of course there also exists a certain coupling between magnetism and ferroelectricity in these materials, but unfortunately it is usually not strong enough, although it was demonstrated, for example, that one can modify the magnetic structure of BiFeO$_3$ by electric field [34].

At the beginning if this century the other, novel class of multiferroics was discovered [22, 23] — the systems which we can call type-II multiferroics. These are the systems in which ferroelectricity exists and is generated only in certain magnetically-ordered states. These materials attract now the main attention from the point of view of fundamental science. They are, however, at least as yet, less promising for practical applications than type-I
systems such as BiFeO$_3$, or composite multiferroics consisting e.g. of layers of nonmagnetic FE such as (PbZr)TiO$_3$ and adjacent layers of good magnets such as permalloy, with the coupling between these layers occurring via common strain (using magnetostriction of magnetic layers and piezoelectric response of FE ones). But from the physical point of view these type-II, or magnetically-driven MF, present special interest$^2$.

6 Type-I multiferroics

The varieties of type-I multiferroics differ first of all by the mechanisms leading to ferroelectricity. Two such types we have already shortly discussed above.

*Systems having structural units with permanent dipoles.* To such systems belong materials containing for example polar groups such as BO$_3$. If there are also magnetic ions in such compounds, these could be multiferroic. Examples thereof are boracites, e.g. the Ni–I boracite Ni$_3$B$_7$O$_{13}$I $^{[15]}$, or iron borate RFe$_3$(BO$_3$)$_4$ $^{[24]}$.

*Hydrogen-bonded ferroelectrics.* As mentioned above, to these systems belong the first known ferroelectric — the Rochelle (or Seignette’s) salt, first prepared in 1675. There are many materials in this class, but there are no good multiferroics yet among those.

*Transition metal perovskites.* Probably the most important class of multiferroics are the systems such as perovskites in which ferroelectricity is due to “FE-active” transition metal (TM) ions. Such are for example the famous BaTiO$_3$. In classical physics one usually describes FE as a consequence of the so called polarization catastrophe, at which the high polarizability of some constituent ions leads to an instability of the nonpolar state and to creation of ferroelectricity. However there is another, more microscopic explanation of

$^2$Sometimes one presents a different classification of MF, paying main attention to the fact whether polarization is a primary order parameter, or whether it is caused by the coupling to another one, for example magnetic ordering, e.g. due to coupling $\sim PM^2$ (but possibly also by coupling to some non-ferroelectric structural distortion). One calls the first class of these systems proper FE, and the second one improper FE $^{[35]}$. In the usual Landau theory of II order phase transitions, see e.g. $^{[36, 37]}$, the primary order parameter $\eta$ close to the critical temperature behaves as $\eta \sim \sqrt{T_c - T}$, but for example for the coupling of the type $P\eta^2$, e.g. $PM^2$, polarization is linear in temperature, $P \sim T_c - T$. 

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the appearance of ferroelectricity in systems such as BaTiO$_3$: the establishment of a strong covalent bond of the transition metal ion, here Ti, with one (or several) of the surrounding oxygens at the expense of weakening the bond with the other ones, see Fig. 5. One can show, see e.g. [3], that the energy gain by the corresponding shift $\delta u$ of Ti ions from the centres of O$_6$ octahedra is $\sim -g(\delta u)^2$. As the elastic energy loss is also quadratic in $\delta u$, $+\frac{1}{2}B(\delta u)^2$, such phenomenon may occur only if the gain of covalency energy exceeds the elastic energy loss, for which one needs strong electron–lattice interaction (large coupling constant $g$ above) and a not too stiff lattice (smaller bulk modulus $B$). These conditions are met not in all materials even with similar structures. That is why for example BaTiO$_3$ is ferroelectric; SrTiO$_3$ is not but is “almost there” (it has a very high dielectric constant, and small perturbations such as uniaxial stress and even isotope substitution $^{16}$O $\rightarrow$ $^{18}$O make it ferroelectric); and CaTiO$_3$ is much further from the ferroelectric state.

![Diagram of O-Ti-O octahedra](image)

**Fig. 5**

However BaTiO$_3$, a classical ferroelectric, is not magnetic, i.e. not a multiferroic. The analysis of experimental data, e.g. the comparison of extensive tables with the large amount of data on ferroelectric [17] and magnetic [18] perovskites shows that usually these two types of ordering in perovskite family are mutually exclusive. Ferroelectricity in “classical” systems is observed practically exclusively in perovskites $ABO_3$ with TM $B$-ions with empty $d$-shells, i.e. with the occupation $d^0$ (BaTi$^{4+}$O$_3$; LiNb$^{5+}$O$_3$ etc.). On the other hand, magnetism requires partial occupation of $d$-levels. The realization of
this dichotomy caused a long debate why this is so, and why none (or so few) magnetic perovskites with $d^n$ ($n \neq 0$) shells are ferroelectric [19, 20, 3]. There are several physical factors proposed to explain this property.

One is simply that the ions with empty $d$-shells are usually smaller than those with $d^n$ ($n \neq 0$) configurations, so that such small ions can easily shift from the centre of a large O$_6$ octahedral cavity. This factor may play a certain role, see below, but it does not explain why for example BaTiO$_3$ is ferroelectric while CaTiO$_3$ is not. Even worse: CaMnO$_3$ is also not ferroelectric, although it contains ions Mn$^{3+}$ which are smaller than Ti$^{4+}$ in BaTiO$_3$ [38].

The other factor could be that, whereas the formation of a strong covalent bond with, say, one oxygen, see Fig. 5, leads to a decrease of the electron energy (only the bonding orbital is occupied for $d^0$ TM ions, Fig. 6(a)), in the presence of real $d$-electron(s) on TM the antibonding orbital should also be filled, Fig. 6(b). Because of that we lose, in this simple example, half of the energy which we gained by shifting the $d^0$ TM ion. This effect, if it does not forbid FE in this case, at least makes it much less probable.

One can think of yet another factor which could suppress the formation of TM–O covalent bonds leading to ferroelectricity, or at least make it less favorable [3]. The covalent bond is a typical singlet chemical bond, e.g. with the wave function of the type $\frac{1}{\sqrt{2}}(d^\uparrow p^\downarrow - d^\downarrow p^\uparrow)$, as in the H$_2$ molecule in the Heitler–London approximation. However in the presence of another localised $d$-electron (or several of those), as in Fig. 6(b), the Hund’s rule exchange would destabilize the singlet covalent bond — similarly to the magnetic pair-breaking of singlet Cooper pairs in $s$-wave superconductors with magnetic impurities [39].

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig6.png}
\caption{Fig. 6}
\end{figure}
All these factors could be at work and make the coexistence of magnetism and ferroelectricity in these systems very unlikely. But one has to realize that this mutual exclusion is not a “theorem”; it is a game of numbers, and the physical factors described above, though making this coexistence highly unlikely, do not forbid it. And indeed, it was predicted theoretically [40, 41] and observed experimentally [42] that in the system $AMnO_3$ with magnetic $Mn^{4+}$ ($d^3, S = \frac{3}{2}$) the system may become ferroelectric when one increases the size of the $A^{2+}$ ions (going from Ca to Sr to Ba).

But probably the more natural route to create multiferroics in perovskites is the route first taken by several groups (see reviews in [43, 44]) — to make a mixed perovskite containing FE-active ions with the configuration $d^0$, and magnetic ions with configuration $d^n$, $n \neq 0$, in the hope that every species will do “what it wants”. And indeed, on this route several multiferroics of this series were synthesized, first by Smolenskii and his group [43]. Some of them were even ferro-, or rather ferrimagnetic, which is very favourable for possible applications. Unfortunately the coupling between magnetic and FE degrees of freedom in these systems turned out to be rather weak.

There are also other suggestions of how to make magnetic perovskites ferroelectric. Thus, one idea is to use the coupling between rotation and tilting of $BO_6$ octahedra often occurring in perovskites $ABO_3$ [45]. And indeed it was possible to create MF on this route. This mechanism, however, belongs rather to another class of FE and MF behaviour which we may call “geometric” mechanism.

“Geometric” multiferroics. As mentioned in the footnote on p. 14, there are many multiferroics with improper FE, in which FE appears as a secondary effect (a “by-product”) of a primary ordering, e.g. of rotation and tilting of structural units in a crystal, such as $MO_6$ octahedra. The best known and the most important examples of systems with this mechanism of FE are the hexagonal systems $RMnO_3$ (where $R$ is a small rare earth ion), e.g. $YMnO_3$. These systems sometimes are called hexagonal perovskites, although they have not much in common with real perovskites except similar-looking chemical formulae. In these systems the $Mn^{3+}$ ions with 5-fold coordination are located in the centres of trigonal bipyramids (two oxygen tetrahedra “glued” together by a common face, common oxygen triangle). They form layered structures with triangular $Mn$ layers. Similar to conventional perovskites, here these building blocks also have a tendency towards tilting and rotation, to guarantee the close packing of the lattice.
such distortions (in perovskites they are called GdFeO$_3$-distortion) there appear short AO pairs with a dipole moment. But in perovskites ABO$_3$ these dipoles in neighboring cells are oriented in opposite directions and cancel each other, and in the standard case they don’t lead to net ferroelectricity (unless one uses special tricks to avoid this compensation). However in systems such as YMnO$_3$ there is no such compensation. The geometric mechanism of ferroelectricity in these systems, which presents a good example of improper ferroelectrics, was established in [46]. These materials, with their interesting magnetic structure, present nowadays an important playground for studying, in particular, the characteristics of multiferroic domains and domain walls.

One extra comment must be made in connection with geometric ferroelectrics and multiferroics. We have explained its origin by the rotation and tilting of building blocks of a system, e.g. MO$_6$ octahedra in perovskites or MO$_5$ trigonal bipyramids in systems such as YMnO$_3$. This one, in its turn, is usually explained by the tendency towards close packing of rigid ions, characterized, for perovskites BO$_3$, by the tolerance factor $t = (R_A + R_O)/\sqrt{2}(R_B + R_O)$: for $t \sim 1$ the system remains cubic, but for smaller values of $t$ there occurs rotation and tilting of the BO$_6$ octahedra, see e.g. [9]. But if we look more deeply, beyond the simplified picture of rigid ions, we realize that it is again a certain tendency of chemical bonds, in this case predominantly $A$–O bonds, which leads to such distortions. Thus in effect it is always local chemistry which is responsible for the formation and stability of one or the other crystal structure, in particular FE one. Very often one can express this tendency in the language of the pseudo-Jahn–Teller, or second order Jahn–Teller effect [47].

**Lone pair mechanism.** Yet another “chemical” mechanism of ferroelectricity is provided by materials containing ions with the so-called lone pairs, or dangling bonds. These are usually materials containing Bi$^{3+}$ or Pb$^{2+}$. Bi typically accepts valences 3+ and 5+. Bi$^{5+}$ has the electronic structure $(\text{Xe})4f^{14}5d^{10}$, and Bi$^{3+}$ has two extra 6s electrons. In principle these could become valence electrons and take part in the formation of chemical bonds (as they do for Bi$^{5+}$). However in Bi$^{3+}$, and similarly in Pb$^{2+}$, these two electrons do not participate in the formation of chemical bonds and are free to “rotate” in different directions in a crystal, which could lead to a particular orientation of dipole moments associated with them. (Of course these are not pure 6s electrons which are spherical, but they are usually hybridized with
their own \( p \)-electrons, or with \( p \)-electrons of surrounding ligands, e.g. oxygens.)

**Ferroelectricity due to charge ordering.** One more mechanism of FE and of eventually MF behaviour is the possibility that the charge ordering (CO), existing in some materials, can break inversion symmetry and lead to ferroelectricity. I will restrict myself to a few remarks illustrating the main idea of this phenomenon.

Suppose we have a structure consisting of dimers with equivalent sites, such as for example \( \text{H}_2 \) molecules, see fig. 7(a). This structure is definitely centrosymmetric and is not FE (the inversion centres are marked in Fig. 7 by small encircled crosses \( \otimes \)). If however we now have an extra intradimer charge ordering, Fig. 7(b), making “left” and “right” ions in a dimer inequivalent, each such dimer (a “molecule”) would have a dipole moment (double arrows in Fig. 7(b)), and the entire system may become ferroelectric. This mechanism was first proposed in [48], and it is now detected in some materials. And if some constituting ions are magnetic, such systems would simultaneously become multiferroic.

![Fig. 7](image)

Concluding this section, a few general remarks are in order. When considering electric polarization, one usually speaks about two contribution to it, the ionic and the electronic contributions. FE transition is always a structural phase transition from the paraelectric phase with centrosymmetric crystal structure to the low-temperature state with lattice symmetry with broken inversion, belonging to a pyroelectric class [11]. As with all structural transi-
tions, besides a shift of ions there is also a redistribution of electron density (actually a change of chemical bonding). Consequently, one can speak about two contributions to the total polarization in ferroelectrics: an ion contribution and an electronic one\(^3\) (although, strictly speaking, it may be impossible to define those rigorously). By electronic contribution we have in mind, more specifically, the FE caused by the change of electronic distribution at fixed positions of ions. Of course, if we then “release” the lattice, the ions would relax and the ionic positions would adjust to the change of electronic density. Still, the main driving mechanism could be predominantly electronic.

Usually these contributions are determined theoretically, for example using ab initio calculations. And the outcome turns out to be not universal, and it strongly depends on the system. Thus, in perovskites \(RMnO_3\) with small rare earth \(R =\) Er, . . . , with the \(E\)-type magnetic structure, ionic and electronic contributions are comparable [49], but in \(TbMnO_3\) the ionic contribution dominates, electronic contribution being only about 10\% of the ionic one (and in opposite direction) [50]. But in principle there can exist situations with polarization of predominantly electronic character, see above and the next section.

7 Type-II multiferroics

By type-II multiferroics we refer to multiferroics in which ferroelectricity exists only in a magnetically-ordered state, and is in fact driven by a particular type of magnetic ordering. It was the discovery of such MF [22, 23] that invigorated the entire field of multiferroics and which made them such a hot topic. From a symmetry point of view we are dealing here with materials in which the crystal structure has an inversion symmetry, i.e. which in themselves are not ferroelectric, but in which a particular type of magnetic ordering breaks this inversion symmetry. As discussed in Sec. 4 above, if in such situation both \(T\) and \(J\) invariance are broken, but the combined \(JT\) invariance is preserved, the systems would be linear magnetoelectrics, but not multiferroics. If, however, the \(JT\) invariance is also broken, the system

\(^3\)Once again, if we look deeper, in effect all cohesion in solids, and consequently all structural transitions, are of electronic nature “deep inside”. Nevertheless it makes sense to separate electronic and ionic contribution to polarization — with the meaning, crudely speaking, that the ionic contribution is predominantly the contribution of ionic cores, electronic contribution being attributed to the change in the distribution of valence electrons.
is (or can become) multiferroic.

Microscopically one can also speak of several different groups of type-II multiferroics. In this introductory text I will give only a short overview of these questions, paying main attention to some more general or more subtle points.

Type-II multiferroics with spiral magnetic structures. Probably the biggest group of type-II multiferroics discovered until now belong to a class of materials with helicoidal or spiral magnetic structure. Such structures are often incommensurate with the underlying crystal lattice, and they present a subclass of spin density wave (SDW) structure. We can have different types of SDW. They can be sinusoidal, with spins perpendicular (Fig. 8(a)) or parallel (Fig. 8(b)) to the wavevector of the SDW. Or they can be helicoidal (spiral) of two types: proper screw, Fig. 8(c), with spins rotating in the plane perpendicular to the wavevector, or cycloidal, Fig. 8(d), with the spin rotation plain containing the wavevector. There may also exist different types of conical structures, two of which are shown in Fig. 8(e), (f). As is shown both experimentally [51] and theoretically [52, 53, 54], in most cases ferroelectricity is produced by the cycloidal magnetic structures of Fig. 8(d). Such are for example MF systems TbMnO$_3$, MnWO$_4$, etc. The polarization of a pair of spins is given in this case by the following expression [52]:

$$P_{ij} \sim r_{ij} \times (S_i \times S_j) \quad (13)$$

where $r_{ij}$ is the vector from site $i$ to site $j$, and $S_i$ and $S_j$ are the spins at corresponding sites. For the cycloidal structure of Fig. 8(d) the polarizations (dipole moments) of consecutive bonds add, producing net ferroelectricity and multiferroic behaviour. In this case one can write down the expression for the total polarization, (13), in the equivalent form [54, 2]

$$P \sim Q \times (S_i \times S_j) \sim Q \times e \quad (14)$$

where $Q$ is the wavevector of the cycloid and $e$ is the axis of rotation of spins in the cycloid. In other words, the polarization of the cycloid lies in the plane of rotating spins and perpendicular to the spiral axis. The same expression also gives the polarization of the conical spiral of Fig. 8(f): the “antiferromagnetic” component of the spins rotates in a cycloidal fashion, and produces polarization given by the same expressions (13), (14).

According to these expressions, the proper screw of Fig. 8(c) or conic spiral of Fig. 8(e) should not produce any polarization. This was indeed the
accepted point of view for some time, until it was realized [55, 56] that in certain cases these magnetic structures can also lead to polarization, in this case directed along the spiral direction $Q$. Indeed, in this case all directions perpendicular to $Q$ are equivalent, and polarization can be directed only along the spiral. But if a crystal has two-fold symmetry axis $C_2$ perpendicular to $Q$ (which was implicitly assumed in the derivation leading to expressions (13) and (14)), then both directions, parallel and antiparallel to $Q$ are equivalent, i.e. $C_2P = -P$, which leads to $P = 0$. However if such two-fold axis in a crystal symmetry is absent, nonzero polarization can in principle exist. And indeed, several MF materials with the proper screw magnetic structure were discovered experimentally [57].
From a microscopic point of view the mechanism of FE and MF in the most common case of a cycloidal structure is the inverse Dzyaloshinskii–Moriya effect [53]. The Dzyaloshinskii–Moriya interaction has the form

$$D_{ij} \cdot (S_i \times S_j) ,$$

(15)

where the Dzyaloshinskii vector $D_{ij}$ for a pair $ij$, in the case of systems with superexchange e.g. via oxygen, Fig. 9, is proportional to the displacement $\delta$ of oxygen from the centre of the $i$–$j$ bond,

$$D_{ij} \sim \delta \times r_{ij} .$$

(16)

This interaction leads to the canting of otherwise collinear spins $S_i, S_j$. But, inversely, if by some reason (most often due to frustrations) the magnetic structure is of a cycloidal type with canted neighbouring spins, it is favourable to shift the oxygens to gain the Dzyaloshinskii–Moriya energy (15). For a cycloidal structure of Fig. 8(d) all such shifts would be in the same direction, which would produce an electric polarization given by the expressions (13), (14).

![Fig. 9](image)

There are also other microscopic mechanisms leading to MF in such cases, e.g. for a proper screw [56]. I will not discuss them here. It is only important to notice that all of them rely on the presence of the (relativistic) spin–orbit interaction $\lambda l \cdot S$, and therefore typically the FE polarization in such cases is rather small. There exists however another mechanism of multiferroicity, not relying on the real spin–orbit interaction and acting also for collinear magnetic structures.

**Magnetostriction mechanism of type-II multiferroics.** Another mechanism of multiferroic behaviour is the standard magnetostriction due to the dependence of the exchange integral $J_{ij}$ on the distance between sites $i$ and $j$, and often also on the angle $M_i$–$O$–$M_j$ for the superexchange mechanism, Fig. 9. Due to this magnetostriction some ions shift in the magnetically-ordered phase, which can lead to electric polarization.
The simplest (and actually realistic) example is shown in Fig. 10 (cf. Fig. 7, with which it has much in common, and also the discussion at the end of Sec. 4). Suppose we have a lattice made of ions with different charges, which in itself is centrosymmetric, Fig. 10(a) (each ion is an inversion centre). If however the magnetic structure is of the type $\uparrow \uparrow \downarrow \downarrow$, Fig. 10(b), then the inversion symmetry would be broken by this magnetic structure, and the material could become ferroelectric. And indeed, due to magnetostriction the ferromagnetic and antiferromagnetic bonds would become inequivalent, and if, for example, the ferromagnetic bond would become shorter, we would get the situation of Fig. 10(c), with polarization shown by the double arrow, $\uparrow$. We see that this mechanism resembles very much that of Fig. 7, where we started with inequivalent bonds and obtained ferroelectricity by putting charge ordering on top. Here we consider an opposite situation: with inequivalent sites, bonds becoming inequivalent due to magnetostriction in a particular magnetic structure. Note that this mechanism works also for a collinear spin structure, and it does not require any relativistic spin–orbit interaction. Therefore one could expect larger values of FE polarization in such systems, and indeed this is the case: if for typical cycloidal multiferroics the polarization is usually $\sim 10^{-2} \mu\text{C}/\text{cm}^2$, in multiferroics with the magnetostriction mechanism it can reach several $\mu\text{C}/\text{cm}^2$. Thus, theoretical considerations predict for Mn perovskites with $E$-type magnetic structure
(resembling somewhat that of Fig. 10(b)) the polarization \( \sim 2 \mu \text{C/cm}^2 \) [49]. The first measurements [58] demonstrated much smaller values, but the improved quality of the samples allowed to reach values almost equal to the theoretical prediction.

Experimentally there exist many multiferroics with this mechanism of ferroelectricity: e.g. one of the very first type-II multiferroics, TbMn\(_2\)O\(_5\) [23, 59]; the material Ca\(_3\)CoMnO\(_6\) [29] which is well described by the structure of Fig. 10; CdV\(_2\)O\(_4\) [60]; and a few others.

Electronic mechanism of ferroelectricity in frustrated magnets. If in the examples of type-II multiferroics considered above the ionic displacements played a crucial role, and the ionic contribution to polarization was significant, sometimes dominant [50] (although the electronic contribution was also important), there exists a possibility of a purely electronic mechanism of MF behaviour. Such mechanism, proposed in [61], see also [62], can operate in frustrated magnets with a particular magnetic structure. One can show that in a magnetic triangle with one electron per site, described by the strongly interacting Hubbard model

\[
\mathcal{H} = -t \sum_{\langle ij \rangle} c_{i \sigma}^\dagger c_{j \sigma} + U \sum_i n_{i \uparrow} n_{i \downarrow} \tag{17}
\]

there would appear, for certain magnetic structures, a charge redistribution, given by the expression

\[
n_i = 1 + \frac{32t^3}{U^2} \left[ S_1 \cdot (S_2 + S_3) - 2S_2 \cdot S_3 \right], \tag{18}
\]

see Fig. 11. If the spin correlation function entering (18) is nonzero, as is the case for the structure of Fig. 11, charge redistribution would occur, and the triangle would acquire a dipole moment (double arrow in Fig. 11). In principle this could give net polarization in a bulk solid consisting of such triangles, see [62], in which case the material would be multiferroic. (Of course, if we then release the lattice, it would also distort somewhat, also contributing to the polarization; but the main mechanism and the driving force of multiferroic behaviour is in this case purely electronic.)

8 Beyond multiferroics

It is a very interesting development that, after learning many things while studying multiferroics, we can go back to some more traditional magnetic
systems, and using the “multiferroic know-how” predict (and observe) many very nontrivial effects connected with the coupling between magnetic and electric phenomena. I will briefly discuss a few of these below.

8.1 Electric activity of magnetic domain walls

The specific features of domain wall in multiferroics such as BiFeO$_3$ or YMnO$_3$ is a very important and well-studied field. Here I want to draw attention to a slightly different aspect. It was first pointed out by Mostovoy [54] that there should exist nontrivial magnetoelectric and multiferroic effects in some domain wall even in ordinary insulating ferromagnets.

Typically, there exist two types of domain walls in ferromagnets: Bloch domain walls, Fig. 12(a), in which spins rotate in the plane of the wall, perpendicular to direction from one domain to the other; and Néel domain wall, Fig. 12(b), in which spins in the centre of the domain wall point alongside the normal to this wall. We immediately see that the Bloch wall presents a part of the proper screw of Fig. 8(c), whereas the Néel wall has a “cycloidal” structure of Fig. 8(d). According to eqs. (13), (14) one should then expect the appearance of electric polarization at every Néel domain wall.

One can then propose a beautiful experiment, which was indeed carried out [63]. It is well known that if we put magnetic dipoles (“magnetic needles”) in an inhomogeneous magnetic field, such needles would be attracted (or repelled, depending on the direction of the dipoles) to the region of stronger field. The same of course is also true for electric dipoles in the gradient of an electric field.

The group of Logginov and Pyatakov [63] carried out such experiment not with the usual magnetic dipoles, but with the insulating ferromagnets with Néel domain walls, which, according to arguments presented above,
should carry electric dipoles. They used a film of a well-known such material, the iron garnet \((\text{Bi,Lu})_3(\text{Fe,Ga})_5\text{O}_{12}\), with \(T_c \sim 450\) K, approached it by a sharpened copper wire and applied a voltage pulse to the wire. This produced an inhomogeneous electric field in the film, see Fig. 13, and it was observed that the Néel domain walls were attracted to the region of stronger electric field. This experiment, besides demonstrating the appearance of electric dipoles on Néel domain walls, opens a way to control such domain wall by the electric field, which may be extremely useful in manufacturing new electrically-controlled memory media and devices.

8.2 Spiral magnetic structures on metal surfaces

Yet another experimental observation which can be easily explained if we invoke the physics described above is the detection of helicoidal magnetic structures in thin films (monolayer, bilayer) of magnetic metals on nonmagnetic substrates [64, 65, 66]. The first such results were obtained on a monolayer of manganese on tungsten [64], see Fig. 14. It was observed that instead of forming a collinear magnetic structure, a cycloidal spiral was formed (Fig. 14 is a
simplified schematic picture, which shows the situation if the Mn layer were ferromagnetic; see the original publication for the actual structure). From what we have learned in Sec. 7, it is clear that the cycloidal spiral would produce a polarization and a corresponding electric field, perpendicular to the surface. But, vice versa, the intrinsic electric field always existing at the surface of a metal (due to the double-charge layer, or the potential drop — the work function of the metal), which is normal to the surface, would have the tendency to create a cycloidal spiral from the initially collinear spin structure. And as this intrinsic electric field in the double layer always has the same sign on the entire surface, all the spirals in such monolayer would have the same sense of rotation, e.g. clockwise.

This phenomenon should be quite general, since such potential drop exists at the surface of every metal. But this tendency to rotate the spins would act against the magnetic anisotropy, always present at the surface, and in order
to be observable it must be strong enough to overcome this anisotropy. This is why such cycloidal structures are found not on all magnetic layers on top of any metal. One needs at least a strong spin–orbit coupling at the surface (we remind that the mechanism leading to (13), (14), is in fact the spin–orbit interaction), for which it is better to use a heavy metal as a substrate; and it is also desirable to have magnetic metals without very strong single-site anisotropy.

The authors of the original papers themselves proposed an explanation which relies on the Dzyaloshinskii–Moriya interaction at the surface [66] (which always exists in this case, since the inversion symmetry is broken by the surface itself). In fact, physically this is the same explanation as the one described above (as mentioned previously, the microscopic mechanism of the relations (13), (14) is in fact the same Dzyaloshinskii–Moriya interaction). However the picture presented in Fig. 14 is simpler and more transparent, even if it is conceptually the same. By the way, the same coupling of magnetic and electric degrees of freedom at the surface, which lies at the core of our picture, is also very similar to the recent proposal [67] explaining the large magnitude of Rashba spin–orbit coupling at the surface by the important role of electric dipoles at the surface layer.

8.3 Magnetoelectric effects on magnetic vortices and skyrmions

There may exist different magnetic textures in normal magnets: not only domain walls, but also, for example, magnetic vortices, Fig. 15(a), (b), or skyrmions, Fig. 15(c).

One can show that all such objects would exhibit a linear magnetoelectric effect [68]. The “head to tail” vortices of Fig. 15(a) are classical examples of systems with toroidal moment \( T \sim \sum_i r_i \times S_i \), shown in Fig. 15(a) by a double arrow. This means that here we would have a ME of the type described in Sec. 6, with e.g. the polarization \( P \) perpendicular to the magnetic field \( H \), \( P \sim T \times H \), and similarly with magnetization \( M \) induced by electric field \( E \), \( M \sim T \times E \). On the other hand, the “radial” vortex of the type of Fig. 15(b) would have a linear ME effect with a symmetric ME tensor \( \alpha_{ij} \), i.e. the polarization would be parallel to the external magnetic field (along the principal directions in which \( \alpha_{ij} \) is diagonal).

Skyrmions (“magnetic hedgehogs”) can be of two types. Most often,
Fig. 15(c), in the “middle part” of a skyrmion the spins are rotating as in Fig. 15(a). In this case the skyrmions would also exhibit transverse ME effect. But in the case of “radial” skyrmions (real “hedgehogs”) the ME would be longitudinal. The ME effect in skyrmions was recently experimentally observed in [69]. Interestingly enough, skyrmions can also be created on magnetic layers on the surface of a metal [70, 71], apparently due to the mechanism described in the previous subsection.
8.4 Electric activity of spin waves

From what we have learned in studying the cycloidal type-II multiferroics, Sec. 7, we can predict yet another interesting effect — electric activity of spin waves [7]. As is well known, see e.g. [9], a quasiclassical picture of magnons in a ferromagnet is the precession of spins along the direction of magnetization, Fig. 16. As we see, in this case the instantaneous picture (a “snapshot”) is that in which the perpendicular $(xy)$ component of magnetization forms a cycloid in $xy$-plane. Consequently, according to our understanding reached in studying type-II multiferroics, eqs. (13), (14), such spin wave should carry, besides magnetization, also an electric dipole perpendicular both to magnetization and to the magnon wavevector $Q$ (double arrow in Fig. 16).

One can also give this effect a completely classical interpretation. It is well-known that there exists a circular magnetic field around a wire carrying a current, Fig. 17(a). Correspondingly, the field of two such wires with currents in opposite directions would produce a magnetic field, or magnetic moment, located between the wires and pointing in the direction marked on Fig. 17 by a double arrow. (The fields far away from the double wire would cancel.) But there exists a well-known symmetry between magnetic and electric phenomena, exemplified best of all by the Maxwell equations. Correspondingly, the motion of a magnetic dipole, which can be represented as a parallel motion of south and north poles, or positive and negative magnetic charges (although such monopoles do not exist separately), would correspond to magnetic currents running in opposite directions, as in Fig. 17(b), and in effect such “currents” created by a magnon — classically the propagating magnetic dipole — would be accompanied by an electric field, or electric dipole shown in Figs. 16, 17(c).


9 Conclusions

In this introductory text I have tried to give an overview of some basic notions and phenomena which we meet in studying this interesting class of materials — multiferroics. Concluding this short overview I only want to stress once again that not only multiferroics themselves present significant interest, both from general point of view and that of practical applications, but also the study of other interesting phenomena in other types of solids benefits strongly from the experience we get in studying multiferroics.

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