Ferroic Materials: A Primer

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The subject of ferroic materials encompasses a large number of topics in materials science in general, and physics in particular. An overall perspective is presented in a simple, reasonably nontechnical language. The vast application potential of ferroic materials is highlighted.

Introduction

Materials possess symmetry, and sometimes they undergo a change of symmetry 'spontaneously' when environmental conditions are changed. For example, water changes to ice on cooling through a certain specific temperature, namely its freezing point. Liquid water has a very high degree of rotational or orientational symmetry: its macroscopic properties are the same in all directions. By contrast, when water changes to ice, which is a crystalline material, there is a drastic reduction in the directional symmetry: most of the macroscopic properties of ice or any other crystal are not the same in all directions. One describes this phenomenon (freezing) as entailing a spontaneous breaking or reduction of directional symmetry.

Spontaneous breaking of directional and other types of symmetry is widely prevalent in Nature. Even the birth of the Universe (at the moment of the 'big bang') was a process of spontaneous breaking of certain symmetries.

In the science of crystals, study of changes of symmetry as a function of temperature, pressure, etc. is a very well-developed subject. When a crystal changes its symmetry, it is a process of going from one phase to another. We therefore speak of a 'phase transition entailing a change of symmetry'. Ferroic crystals are those crystals which involve at least one phase transition which changes the directional symmetry of the crystal. The term 'ferroic materials' is a general term covering ferromagnetic

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materials, ferroelectric materials, ferroelastic materials, ferrogyrotropic materials, etc.

Ferromagnetic Materials

Let us consider a crystal of iron. At high enough temperatures, it is in what is called a paramagnetic phase. Application of a magnetic field to it induces a response in the form of a magnetic moment, and the magnitude of the magnetic moment induced by the applied field is proportional to the magnitude of the field applied. The response function in this case is a 'single-valued function': there is a unique value for the induced magnetisation for every value of the field applied.

When a crystal of iron is cooled, there comes a temperature at which it makes a phase transition to what is called a ferromagnetic phase. In this phase the crystal has a nonzero magnetic moment even when no external magnetic field is applied to it; we call this magnetic moment, for obvious reasons, 'spontaneous magnetic moment' or 'spontaneous magnetisation'. The existence of this spontaneous magnetisation also implies that the crystal has a lower directional symmetry (or a lower 'point-group' symmetry) compared to that of its paramagnetic phase. So this is another case of spontaneous breaking of symmetry.

There are several consequences of this spontaneous breaking of symmetry, but we shall first focus on only one of them here. When spontaneous magnetisation arises in iron, there is no reason why its direction should be the same in the entire crystal. There can be at least two such 'equivalent' directions. In other words (assuming that this number is only two), some regions of the crystal may have their spontaneous magnetic moment pointing in a particular direction, and some others may have it pointing in the opposite direction. A geometrical analogy will help explain why this should be so:

Imagine a square, two sides of which are vertical, and the other two horizontal. Suppose it undergoes a spontaneous reduction of symmetry, and becomes a rectangle. This can happen in two

ways: either the vertical pair of sides elongates and the other pair contracts, or vice versa. So we end up getting two possible 'orientation states': those in which the rectangle is vertical and those in which it is horizontal.

The different orientation states in a crystal are also called 'domain states'. Thus a crystal of iron, on undergoing a symmetry-breaking transition to the ferromagnetic phase, splits into domains. All parts of a particular domain have the same direction for the spontaneous magnetisation, and different domains can have different directions of spontaneous magnetisation. The total number of such distinct directions is at least two, but can be higher. In fact there is a general theorem, from which it follows that the larger the reduction of symmetry at a phase transition, the larger is the number of distinct orientation states permissible in the lower-symmetry phase.

Thus a crystal of iron in its ferromagnetic phase can have domain structure, with magnetic moments of domains pointing in different directions. Suppose we apply a magnetic field to such a specimen. The applied field has a specific direction chosen by us. Depending on the magnitude of the field applied, several different responses can ensue from the specimen [1]. But the main result is that, if the field applied has a large enough magnitude, then those spontaneous magnetic moments which are oppositely or nearly oppositely oriented with respect to the direction of the applied field will flip or switch to directions parallel or nearly parallel to the field direction. For a large enough field, practically all the magnetic moments will point along directions close to that of the applied field.

Next we start decreasing the applied field. The magnetic moment of the specimen will start decreasing. But even when the applied field is brought down to zero, the specimen crystal will exhibit a nonzero 'remanent' magnetisation (because the crystal structure possesses spontaneous magnetisation). We would have to apply a field of sufficient magnitude in the opposite direction to make the net magnetisation zero. A further and sufficient

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increase in this oppositely applied field will make almost all the magnetic domains point along, or almost along, this new direction of the field.

A decrease in the magnitude of the oppositely applied field to a zero value will leave the specimen with a nonzero remanent magnetisation, but in an opposite direction to that of its previous remanent configuration at zero applied field. We end up with the conclusion that, depending on the history of the specimen crystal, the remanent magnetisation is of positive or negative sign, and even of variable magnitude. Thus the magnetisation is no more a single-valued function of the applied field. This behaviour, brought about by the existence of one or more domain states, is called 'hysteresis' (*Figure* 1).

Spontaneous magnetisation can be exhibited, not only by crystals of elemental iron, but also by crystals in which iron is a constituent of the molecules comprising the crystal. An example is that of loadstone (Fe_3O_4). The world's first compass, using loadstone, was invented in the first century AD, and this invention had far-reaching consequences for the history of mankind, as it made navigation on the high seas possible. Use of ferromagnetic and related materials has also made a major impact on human progress and welfare in the following three areas: generation and distribution of electric power; data storage and processing; and telecommunications. Some of the materials used in these applications are iron-silicon alloys, ferrites and garnets.

Spontaneous magnetisation, and the concomitant domain structure and hysteresis, can be exhibited, not only by crystals con-

Figure 1. Ferroic materials exhibit hysteresis. Shown here are typical hysteresis curves for, respectively, a ferroelectric, a ferromagnetic, and a ferroelastic material. These three types of ferroics are called 'primary' ferroics.
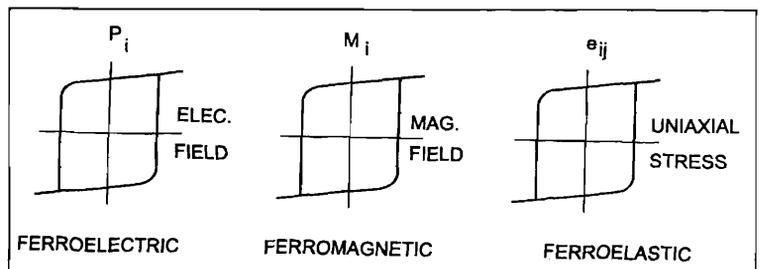
taining iron, but also, for example, by those containing nickel or cobalt. The term 'ferromagnetic behaviour' is used in a general way for all of them, even when iron is not present.

Ferroelectric Materials

The electrical analogue of the phenomenon of ferromagnetism was discovered in 1920, when it was found that crystals of Rochelle salt (sodium potassium tartrate tetrahydrate) possess spontaneous polarisation, the direction of which can be reversed by the application of a strong enough electric field. This property was called 'ferroelectricity', by analogy with ferromagnetism (even though no iron or spontaneous magnetisation is present in the crystal).

A more familiar, and simpler, example of a ferroelectric crystal is barium titanate, $BaTiO_3$. Above 130°C it has a crystal structure such that a macroscopic polarisation (i.e. electric dipole moment per unit volume) can arise in it only when an electric field is applied. This is a 'paraelectric' phase, and the polarisation is a single-valued function of the applied electric field. The directional symmetry of this phase is the same as that of a cube. On cooling below 130°C there is a phase transition to a crystal structure in which the centroids of the positive charges and the negative charges do not coincide, so there is a net dipole moment or polarisation, even when no external electric field is present. This spontaneous polarisation can point along any of six equivalent directions (parallel or antiparallel to any edge of the cube which is the repeat unit for the crystal structure of the paraelectric phase or the parent phase), giving rise to the possibility of six ferroelectric domain types. So we once again get hysteresis when we plot the net macroscopic polarisation of a specimen crystal as a function of increasing and decreasing electric field.

The six orientation states or domain states are equally stable. This means that if a part of the ferroelectric crystal is in a particular orientation state, there is no reason why it should, on

If a part of the ferroelectric crystal is in a particular orientation state, there is no reason why it should, on its own free volition, want to switch to another domain state.

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its own free volition, want to switch to another domain state. One of the very active areas of current research is to exploit this property for storage of information in computer memories and other memories. Thin films, rather than bulk single crystals, of ferroelectrics are more suitable for this application. And compared to barium titanate, some of the more suitable ferroelectrics are barium strontium titanate (BST), lead zirconate titanate (PZT), and lanthanum-doped bismuth titanate (BLT). The 'up' and 'down' states of the spontaneous polarisation in a ferroelectric domain provide the basis for the 0/1 binary logic used in the memory device. And since the 0 and 1 states are equally stable, there is no need to apply a biasing electric field to make a memory-configuration 'nonvolatile'. This is particularly useful for applications in smart cards. NVFRAMs (nonvolatile ferroelectric random-access memories) may eventually replace many of the existing memories in computer applications [2]·

Another likely application of ferroelectric thin films in computers is for making DRAMS (dynamic random-access memories). These will exploit another important aspect of ferroelectric materials, which we have not discussed so far, namely a usually high dielectric permittivity in the vicinity of the ferroelectric phase transition. High permittivity is preferred for making capacitors, because it enables us to reduce the size of the capacitor.

Dielectric permittivity is a 'response function': it is a measure of how large is the response, namely induced polarisation, when a given electric field is applied to the material. For many ferroelectrics, this response function becomes particularly large when the material is at or near the temperature of the ferroelectric phase transition. An analogy from sociology may help explain why this should be so. When things are in a state of flux (say, when there a revolution under way, or a war is going on), even a small trigger (e.g. a rumour) can evoke an unduly large response. During a phase transition a crystal is in a state of great upheaval, and certain small perturbations can invoke an unduly large response.

Similarly, many applications of ferromagnetic materials are based on their high magnetic permeability.

Ferroelastic Materials

There must be a mechanical or elastic analogue of ferromagnetism and ferroelectricity, and this property is called ferroelasticity. A ferroelastic material has spontaneous strain and the concomitant domain structure, as a consequence of which we observe hysteresis when the bulk spontaneous strain is plotted as a function of applied directional stress.

Apparently, ferroelasticity was first discussed by physical metallurgists in the early 1950s in the context of the 'rubberlike' behaviour of gold-cadmium and indium-thallium alloys. In physics, a formal description of ferroelasticity as an independent property in its own right, which can exist even when there is no accompanying property of ferroelectricity or ferromagnetism, and even when no defects (like hydrogen in metals) are present in the crystal, was given by the Japanese scientist Aizu in 1969 [3].

We can understand ferroelastic behaviour in a simple way by going back to the case of spontaneous distortion of a square to a rectangle, mentioned earlier in the article. We say that the rectangle has spontaneous strain (i.e. strain occurring without the application of any mechanical stress) with respect to the square. A three-dimensional version of this would be a cube distorting to a square prism. In fact, this is exactly what happens in the case of the ferroelectric phase transition in barium titanate, mentioned above. So this is not only a ferroelectric phase transition, but also a ferroelastic phase transition. The dimensions of the square prism differ only slightly from those of the cube from which it originated: one edge is longer than the cube edge, and the other two are shorter than the cube edge. And the longer edge can be along any of the three possible (and mutually perpendicular) directions. Thus three distinct ferroelastic orientation states are possible (in contrast to the fact that the

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number of possible *ferroelectric* orientation states in the same phase is six). If we apply a sufficient amount of compressive stress along the longer edge, it would lead to a switching to an alternative orientation state in which one of the other two edges becomes long. So we can expect, and indeed get, stress-strain hysteresis.

Ferroic Materials

It is clear from the above description that there are several common features among materials exhibiting the properties of ferromagnetism, ferroelectricity, and ferroelasticity, the most notable being the occurrence of domain structure (a consequence of spontaneous breaking of symmetry), and the resultant hysteretic behaviour. Aizu therefore coined the general term 'ferroic materials' for all such materials. It should be clear that, although 'ferro' has been used for coining the word 'ferroic', it has nothing to do with the presence or absence of iron in a ferroic material.

Apart from domain structure, a second important feature of a ferroic material is the high value certain response functions of the material can acquire in the vicinity of the ferroic phase transition. A third significant feature is the very large temperature dependence of certain macroscopic properties in the vicinity of the ferroic phase transition. Fourthly, if there is a strong coupling between these properties and other properties, then the latter also behave in a similar way. These four features form the basis of a large variety of device applications of ferroic materials [1].

An important contribution of Aizu is the introduction of the notion of 'prototype symmetry' in the context of ferroic phase transitions. The symmetry of any ferroic phase of a material can be regarded as derived by a small distortion of the prototype symmetry. For example, the symmetry of the cubic phase of barium titanate is the prototype for its 'tetragonal' ferroelectric-ferroelastic phase occurring at room temperature. The cubic

phase is also the prototype for the other phases which occur when the tetragonal phase of barium titanate is cooled still further.

Aizu also realised that there can be various other types of ferroic materials. Let us consider a familiar example. We have this gadget in a modern kitchen which lights up a gas cooker with a spark generated by a battery-less lighter. It consists of a suitably processed piece of a ceramic of lead zirconate titanate (PZT for short). When this ceramic is hit in a hammer-like action, it develops an electric polarisation, with the accompanying surface charge. It is this charge which results in sparking in air. This property of generation of electric dipole moment on application of mechanical stress is called piezoelectricity. Materials exhibiting this property are likely to be 'ferroelastoelectrics', provided one can identify or imagine an acceptable prototype symmetry (as indeed one can in the case of PZT).

Some other types of ferroic properties, identified by Aizu, are ferromagnetoelasticity, ferromagnetoelectricity, ferrobielasticity, etc. Quartz is a familiar example of a crystal which is ferrobielastic; it also happens to be ferroelastoelectric.

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Smart Structures and Materials

It is worthwhile to emphasise another important feature of ferroic materials. It was stated above that some macroscopic properties of ferroic materials may become very large in the vicinity of the ferroic phase transition. Linked to this is the fact that these properties vary very rapidly and nonlinearly with, say, temperature. It can be shown that this results in a field-dependence of these properties [1]. In other words, one can fine-tune these macroscopic properties (for a given purpose in mind) by applying a suitable bias field. This fact can be exploited in the construction of what are called 'smart structures' or 'smart materials'. What is smart about them is that, instead of having fixed properties, they can change their properties in a pre-designed way for serving some useful purpose [1].

Adaptive learning can also be incorporated in the device applications of what are called 'actively smart' structures by the use of fast, real-time, information processing arrangements involving neural networks [4].

Exciting developments can be expected in the area of smart materials and structures in the near future. Investigations on ferroic materials can thus pay rich dividends.

Suggested Reading

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Resonance, Vol.7, No.6, p.91, 2002

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