FERROELECTRIC CRYSTALS

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PREFACE

Forty years have elapsed since the discovery of the dielectric phenomenon
known today under the name of ferroelectricity. Most of our knowledge in this
branch of Solid State Physics has been acquired in the years prior to 1950 through
extensive investigations of three ferroelectric materials: Rochelle salt, potassium
dihydrogen phosphate, and barium titanate. In the last decade the major progress
in the field stems from the discovery of a greater number of ferroelectric crystals.
Unfortunately our knowledge of the basic phenomenon has not been appreciably
enhanced. Hence, a comprehensive treatment of ferroelectricity is very difficult,
if not impossible, at the present stage.

In contrast to some other branches of Solid State Physics, the understanding
of the physical properties of ferroelectric crystals requires a wide range of experi-
mental and theoretical approaches. The large reversible polarizations of these
materials have both electronic and ionic origins. The latter indicates the very
close interdependence between ferroelectric activity and crystal structure. This
interdependence makes the most refined structural analysis a very essential
tool for the investigation of the materials. On the other hand, the existence of
linear electromechanical effects, which require the consideration of interactions
between electrical and mechanical quantities, makes the treatment of the ferro-
electric phenomenon much more complex than, for example, that of the ferro-
magnetic analogue.

Several review articles and monographs have already been written by a number
of authors on the subject of ferroelectricity. All these publications have been
of invaluable help to us at various stages of the preparation of the present mono-
graph. In particular, we have been repeatedly enlightened by the excellent review
article published by Devonshire in 1954, which is, we believe, the best presen-
tation of the ferroelectric phenomenon given to date. The most recent contri-
butions are Megaw's book and Känzig's article, both published in 1957. A large
number of ferroelectric materials have been discovered since, and are discussed
in the present monograph to the extent to which pertinent information is available.

This monograph purports to present the state of the art in the spring of 1960,
with the hope that it serves a dual purpose. First, it may be of help to graduate
students and research scientists unfamiliar with the subject as an introduction
to the problems in the field of ferroelectricity. To attain this goal we have included
several sections of an introductory nature. As the second purpose this monograph
should be useful as a reference work for researchers in the field. It is mainly with
this idea in mind that we have adopted a presentation in terms of chapters and
sections devoted to one compound at a time and we have tried to quote as many
numerical results as we think may be desirable. In a presentation of this kind
repetitions are often unavoidable; nevertheless, we have tried to int

number of cross references to help the reader interested in the continuity of a given phenomenon rather than the characteristics of a given compound.

The science of ferroelectricity has been expanding very rapidly and it is difficult to predict what its future will be. This high rate of expansion can be explained in part by the attractiveness of the bistable characteristics of ferroelectric materials and their resultant device applications. This device potentiality has not been realized, at least until now, but it has stimulated a number of excellent experimental and theoretical investigations of far-reaching scientific interest.

The volume of literature published on this subject is so large that a claim of completeness for our bibliography would be ill advised. While exercising some discrimination, we have tried to compile as complete a list of references as possible up to May 1960. Some of the papers published after this date have also been referred to, although they could not be properly co-ordinated. Lists of literature references are given at the end of each chapter and are arranged alphabetically according to the first letter of the name of the principal author. Researchers in the field of ferroelectricity will have noticed a marked increase in Russian literature in the most recent years. We have also tried to include the Russian contributions in our list of references, but unfortunately linguistic problems did not permit us to digest all the pertinent papers. Our quotations refer to the original Russian periodicals and not to existing translations published by the American Institute of Physics.

F. JONA

December, 1960   G. SHIRANE

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INTRODUCTION

1. General Features of Ferroelectric Crystals

THE MAIN problems which arise in the theory of dielectric crystals are concerned
with the polarization that can be induced in such non-conducting materials
by means of an externally applied electric field. The polarization values which
can be measured in normal dielectrics upon application of experimentally attain-
able fields are usually small. Consequently, the effects that the polarization is
expected to have on a number of physical properties of the crystals, such as
the elastic, optical, thermal behavior, etc., are too small to be observed. For-
tunately, a rather large, but yet limited, number of crystals exhibit polarization
values which are many orders of magnitude larger than those observed in most
dielectrics. The detailed study of some of these crystals has revealed many peculiar
effects which are interesting not only from the point of view of dielectric theory,
but also from that of crystallography, crystal-chemistry, thermodynamics, and,
last but not least, practical applications in the field of electrical engineering.

It has become customary to call "ferroelectricity" the phenomenon exhibited
by these crystals, and "ferroelectric" the crystals themselves. The reason for
this denomination is historical and is due to a formal similarity of the ferro-
electric phenomenon with that of ferromagnetism. The similarity is mainly
phenomenological: just as ferromagnetic materials exhibit a spontaneous magne-
tization and hysteresis effects in the relationship between magnetization and
magnetic field, ferroelectric crystals show a spontaneous electric polarization
and hysteresis effects in the relation between dielectric displacement and electric
field. This behavior is mostly observed in certain temperature regions delimited
by transition (or Curie) points above which the crystals are no longer ferro-
electric and show normal dielectric behavior.

Examples of typical ferroelectrics are: potassium di-hydrogen phosphate,
KH_2PO_4, and a number of isomorphous phosphates and arsenates; barium
titanate, $BaTiO_3$, and other isomorphous double oxides; Rochelle salt (sodium
potassium tartrate tetrahydrate, $NaKC_4H_4O_6 \cdot 4H_2O$), and a few isomorphous
crystals. The properties of these and other ferroelectrics will be discussed in detail
in the following chapters. Reviews of these properties and the problems involved
in the field of ferroelectricity are already available in the articles of Känzig (K 1)
and Forsbergh (F 1) and in the book of Megaw (M 1). These authors follow dif-
ferent approaches in order to accomplish the task. Both Känzig and Forsbergh
treat the problem of ferroelectricity in terms of the *properties* which characterize

the phenomenon. Megaw, on the other hand, presents her description of ferro-electricity in terms of *compounds*, rather than properties, and is particularly concerned with the crystallographic aspect of the problem. Our own approach, in the present treatment of the same problem, is to describe the properties of the various ferroelectric crystals individually, and to emphasize the *dielectric* character of the ferroelectric phenomenon as judged from the viewpoint of the solid-state physicist.

In order to describe the essential features of the ferroelectric phenomenon, let us introduce a model of a hypothetical ferroelectric crystal and see what kind
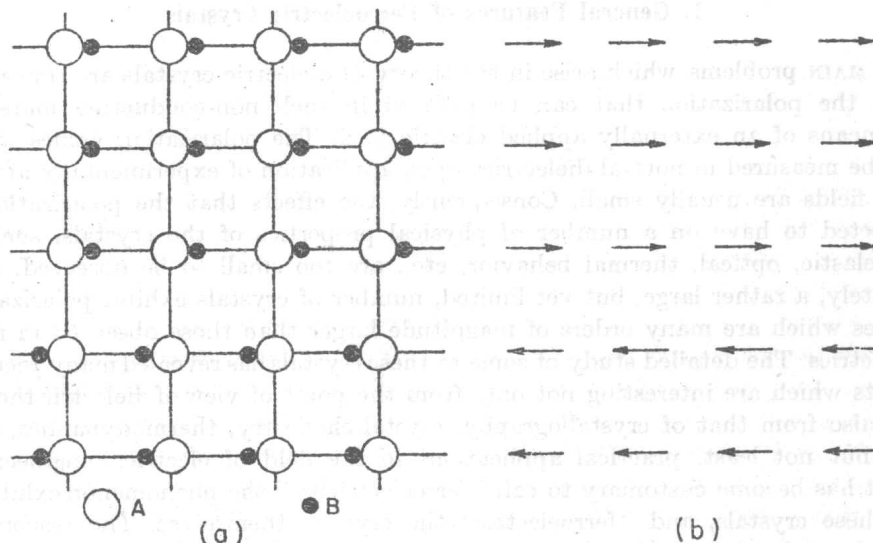
FIG. I-1. Schematic structure of a fictitious ferroelectric crystal.

of dielectric behavior it would show. The model, which has, of course, no general validity and is extremely oversimplified, is that of a two-dimensional crystal having the chemical formula AB and a fictitious structure depicted in Fig. I-1 (a).

The A ions, which we will assume to carry a negative charge, are located on the lattice points of a simple square net. The B ions, carrying a positive charge, are located on the horizontal lines joining the A ions; their equilibrium positions are such that they always lie closer to one of the two adjacent A ions than to the other. Such a situation is possible if the potential between two adjacent A ions is of the type sketched in Fig. I-2 (a): there are two equilibrium positions, corre-sponding to the same minimum value of the energy, for a B ion on the line joining two A ions. The B ions can jump from one equilibrium position to the other but in order to do so they must be provided with the energy necessary to over-come the energy barrier ΔE.

Suppose now that, at a given temperature T, all B ions are closer to their A partners on the left. We can visualize every group AB as an electric dipole and the structure can then be schematically represented by an assembly of dipoles

pointing all in the same direction, as in the three upper rows of Fig. I-1 (b). We say that the crystal is *spontaneously polarized*: the *spontaneous polarization* is measured in terms of dipole moment per unit volume, or, with reference to the charges induced on the surfaces perpendicular to the polarization, in terms

FIG. I-2. Schematic potential wells.

of charge per unit area. The crystals having a spontaneous polarization are called *pyroelectric* (see Section 3) and the direction of the spontaneous polarization is called the *polar axis*.

Alignment of the electric dipoles may extend only over a region of the crystal, while in another region the direction of the spontaneous polarization may be reversed, as in the lower portion of Fig. I-1 (b). Such regions of uniform polarization are called *domains*, a term borrowed again from ferromagnetism. We are going to see in the following that energy considerations require the formation of domains.

Suppose now that we apply an electric d.c. field in the horizontal direction of Fig. I-1. The dipoles which are already oriented in the direction of the field will remain so aligned, but those which are oriented in the direction opposite (antiparallel) to the field will show a tendency to reverse their orientation. If the applied field is sufficiently large, the B ions of our model will be able to overcome the barrier ΔE, and in so doing will cause the corresponding dipole to flip (or switch) over into the direction of the field. This phenomenon of polarization reversal takes place by way of a nucleation process and domain–wall motions. The question which immediately arises is this: how does the process of polarization reversal affect the relation between polarization P and applied electric field E?

Suppose that our crystal is initially composite of an equal number of positive and negative domains (i.e. domains oriented to the right and domains oriented to the left), which means that the overall polarization of the crystal is equal to zero. If we first apply a small electric field directed say, in the positive direction, we will have only a linear relationship between P and E because the field is not large enough to switch any of the domains and the crystal will behave like a normal dielectric. In the plot of P vs. E, shown schematically in Fig. I-3, we obtain the portion OA of the curve. If we increase the electric field strength, a number of the negative domains will switch over in the positive direction

the polarization will increase rapidly (portion AB), until we reach a state in which *all* the domains are aligned in the positive direction: this is a state of saturation (portion BC) and the crystal consists now of a single domain.
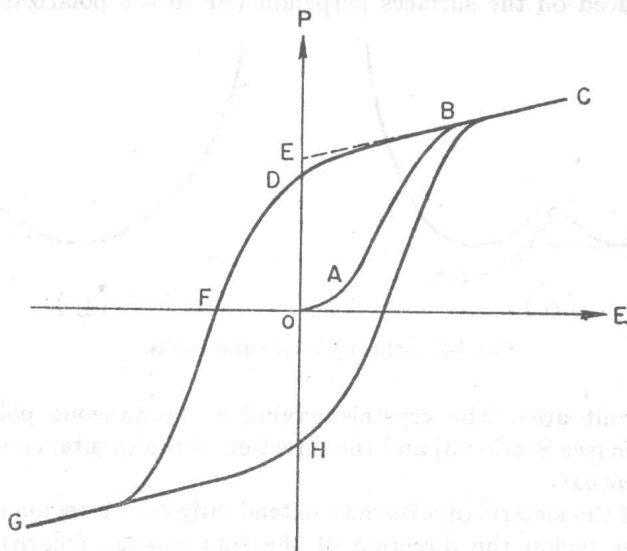
Fig. I-3. Ferroelectric hysteresis loop (schematic).

If we now decrease the field strength, the polarization will generally not return to zero but rather follow the path CD of Fig. I-3. When the field is reduced to zero, some of the domains will remain aligned in the positive direction and the crystal will exhibit a *remenant polarization* $P_r(OD)$. The extrapolation of the linear portion BC of the curve back to the polarization axis represents the value of the *spontaneous polarization* $P_s(OE)$.

In order to annihilate the overall polarization of the crystal, we find it necessary to apply an electric field in the opposite (negative) direction. The value of the field required to reduce P to zero (OF) is called the *coercive field* E_c. Further increase of the field in the negative direction will, of course, cause complete alignment of the dipoles in this direction (FG), and the cycle can be completed by reversing the field direction once again (GHC).

The relation between P and E is thus represented by a *hysteresis loop* $(CDGHC)$, which is the most important characteristic of a ferroelectric crystal. The essential feature of a ferroelectric is thus *not* the fact that it has a spontaneous polarization, but rather the fact that this spontaneous polarization can be reversed by means of an electric field. It may be noted that, owing to the relation between dielectric displacement D, electric field E, and polarization P,

$$D = E + 4\pi P,$$

the relation between D and E is also characterized by a hysteresis curve. The analogy with the well-known ferromagnetic hysteresis loop representing the relation between magnetic induction B and magnetic field H is obvious.

pointing all in the same direction, as in the three upper rows of Fig. I-1 (b). We say that the crystal is *spontaneously polarized*: the *spontaneous polarization* is measured in terms of dipole moment per unit volume, or, with reference to the charges induced on the surfaces perpendicular to the polarization, in terms
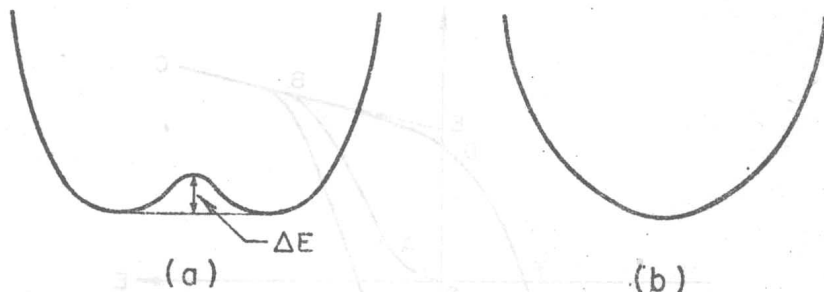

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able to overcome the energy barrier ΔE without the help of an external field, and may therefore jump from one equilibrium position to the other.

Another possibility is that the shape of the potential curve between adjacent A ions changes to the point of becoming as indicated schematically in Fig. I-2(b). In the latter case, there is only one equilibrium position possible for the B ions, i.e. midway between two A ions. In the former case, the statistical distribution of the B ions will be symmetrical with respect to the A ions. The result is the same: our crystal is no longer polar, and will behave rather as a normal dielectric material.

The temperature at which such a transition from the polar into the non-polar state occurs is often referred to as *Curie temperature* (or *Curie point*), again in analogy with ferromagnetism. Almost all ferroelectric crystals known to date have a Curie point, and those which do not have it simply decompose before such a temperature is reached.*

Another consequence of the small atomic shifts occurring in ferroelectric crystals is the behaviour of the dielectric constant of these crystals as a function of temperature. The dielectric constant is normally defined as the derivative of the dielectric displacement D with respect to the field E. Similarly, the derivative of polarization P with respect to field E is usually defined as the dielectric susceptibility k. Owing to the well-known relationship between D, E and P:

$$D = E + 4\pi P,$$

the dielectric constant ε is related to the dielectric susceptibility k, in the c.g.s. system, through the equation

$$\varepsilon = 1 + 4\pi k.$$

This definition of the dielectric constant is significant and consistent for normal dielectrics in which the relationship between D and E is linear up to large values of E. In the case of ferroelectric crystals, ε must be defined more precisely, owing to the more complicated relation between D and E (Fig. I-3). For our purposes, we are going to define the dielectric constant ε as the slope of the D–E curve at the origin:

$$\left(\frac{\partial D}{\partial E} \right)_{E=0}$$

and we are going to measure it with very small a.c. fields, so as not to reverse any domains.

As the potential curve between two adjacent A ions of our crystal changes with temperature, the polarizability of the B ions moving within such a curve will change accordingly. It is thus to be expected that the dielectric constant ε

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* It has become customary, in many publications, to refer to the phase above the Curie point as to the "paraelectric" phase; ferroelectric crystals are, therefore, often said to become "paraelectric" above their Curie temperature. This term originates again from the formal similarity with the behaviour of a ferromagnetic crystal becoming paramagnetic above its transition point. We prefer, however, to refrain from usage of such a term, and we will refer to the state of a ferroelectric crystal above its Curie temperature as the "non-polar" state.

will exhibit some kind of anomaly at the transition temperature. Generally, any kind of phase transition in dielectrics is accompanied by an anomaly of the dielectric constant; a ferroelectric transition, being generally a transition from a polar into a non-polar phase, is no exception to this rule. In some ferroelectrics, the temperature dependence of the dielectric constant above the transition temperature can be described fairly accurately by a simple law, called the *Curie–Weiss law* from its ferromagnetic analog:

$$\varepsilon = \varepsilon_0 + \frac{C}{T - T_0}$$

where the temperature-independent part ε_0 can often be neglected, C is the *Curie constant* and T_0 the *Curie–Weiss temperature*. It is advisable, in general, to distinguish between this Curie–Weiss temperature T_0 and the Curie (or transition) temperature T_c.

In the vicinity of the Curie–Weiss temperature, the dielectric constant becomes very large, and the relationship between dielectric constant and susceptibility can be approximated by

$$\frac{\varepsilon}{4\pi} \cong k.$$

We are going to see in the following that in certain ferroelectrics (which undergo a transition of the second order) the Curie–Weiss temperature T_0 practically coincides with the transition temperature T_c, but in others (which undergo a transition of the first order) it does not. It must be emphasized that a hyperbolic dependence of the dielectric constant on temperature, such as the Curie–Weiss law, is by no means a necessary condition for a ferroelectric transition, as it was customary to believe in the early stages of ferroelectric research. The fact that in some ferroelectrics the anomaly of the dielectric constant is large and the Curie–Weiss law is obeyed may simply mean that the co-operative phenomenon leading to ferroelectricity has a dielectric origin in these crystals, while in others it may have a different character. As we are going to see in the following, a number of characteristic quantities other than the dielectric constant may exhibit anomalies at the transition temperature. This point will be better discussed when we treat specific cases.

2. Spontaneous Polarization

There are a number of fundamental inaccuracies in the description of the model which we have introduced in the preceding section, in spite of the fact that it helps to account for the general features of ferroelectric crystals.

In the first place, we have arbitrarily picked out pairs of atoms and attributed to each of them a dipole moment, defined, as is customary, as the product of charge and separation. This procedure is definitely not legitimate in a real structure. It is true that in a ferroelectric crystal every unit cell carries a dipole moment, but we cannot generally attribute this dipole moment to a specific pair of atoms in the unit cell without making arbitrary assumptions about the interatomic forces.

All we can say is that, given a charge distribution $\varrho(r)$ within a given crystal, the electric moment with respect to an *arbitrary* origin,

$$\iiint \varrho(r) \cdot r \cdot dv,$$

is different from zero and the value of this volume integral is independent of the choice of the origin. To attribute this electric moment to a given pair of atoms would imply that this atomic pair is held together by forces which are stronger than those which bound it to the rest of the structure. This implication is incorrect, because the two atoms which we have picked out are bound to their neighbors by the same forces as those that bind them to each other.

A second important point which does not appear clear in the simple model introduced before is that the dipole moment of each unit cell does not consist only of ionic charges. Eventually, charge separation may occur through the distortion of the electronic cloud of a given atom. In other words, the charge distribution $\varrho(r)$ within the crystal involves not only the ionic but also the electronic charge. Although a distinction between these two contributions to the electric moment is experimentally quite difficult, the concepts of ionic and electronic polarization have been introduced often in the literature. It may be pointed out that these concepts constitute a very important difference between ferroelectricity and ferromagnetism. In ferroelectric crystals, the dipoles are imbedded in a highly polarizable medium ("background"), whose polarizability is temperature dependent, while in ferromagnetic crystals the magnetic moments due to the spin cannot be influenced by the "background".

It should also be pointed out that the simple model introduced in Section 1 is mainly concerned with phenomenological consequences of a spontaneous polarization which is somehow assumed to be already existing within the crystal. We have, in other words, approached the problem of ferroelectricity from the point of view which assumes an already *polarized* state. What we should also do, however, is to follow the opposite approach, starting from the *unpolarized* state, and inquire about the interatomic forces which are at work to bring about spontaneous polarization in a crystal lattice. This problem is of fundamental importance in the general theory of dielectrics, and the reader may be referred, for the details of the following arguments, to the textbooks of Böttcher (B 1), Brown (B 2), Dekker (D 1), Fröhlich (F 2), Kittel (K 2), or Smyth (S 2).

Given a particular type of atom in a substance, we define the polarizability α of such an atom as the ratio between the dipole moment (permanent or induced) of the atom and the electric field acting upon it:

$$\alpha = \mu/F.$$

The field F is generally given by Lorentz's formula for the internal field acting on a dipole located in a lattice of *equal* dipoles with *cubic* symmetry:

$$F = E + \frac{4\pi}{3}P.$$