Pierre Curie's works in the field of crystal physics (on the one-hundredth anniversary of the discovery of the piezoelectric effect)

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In connection with the one-hundredth anniversary of the discovery of the piezoelectric effect by the brothers Pierre and Jacques Curie, the history and principal directions of development of the symmetry principle of Pierre Curie, and of subsequent investigations of piezoelectric and related properties of crystals are briefly analyzed in the present note.

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One hundred years ago in 1880, a short note by the brothers Pierre and Jacques Curie appeared in the journal Comptes Rendues entitled "Appearance of polar electricity under the action of pressure in hemihedral crystals with slanted faces" (Ref. 1, p. 9). At the time, Pierre Curie was twenty-one years old and this was his second scientific publication, informing the world of the discovery of a new physical phenomenon in crystals: piezoelectricity. The Curie brothers wrote:

"We have discovered a new method for the formation of polar electricity in the same crystals (the discussion concerned pyroelectric-crystals-V.K.). This method consists of the fact that the latter crystals are subjected to an alternating pressure in the direction of their hemihedral axes (polar axes-V.K.)...". ...Our experiments were conducted with zinc blende, sodium hypochlorite, boracite, tourmaline, quartz, calamine, topaz, *d*-tartaric acid, sugar, and Seignette salt. In all these crystals, the phenomena induced by compression are the same as in the case of cooling: when the compression is removed, the phenomena occur in the same direction as in the case of heating. There is an obvious relation here, which permits ascribing the phenomenon in both cases to the same cause and to unify them with the following assertion:

Whatever the reason, each time when a hemihedral nonconducting crystal with slanted faces is compressed, an electrical polarization arises with a certain orientation: each time that this crystal is stretched, electricity is generated in the opposite direction. If this point of view is correct, then the phenomena created by compression must have the same direction as those that stem from heating in substances that have a negative coefficient of expansion along the hemihedral axis."

In her recollections of Pierre Curie, Marie Curie writes (Ref. 2, p. 17): "This discovery was not accidental. It was arrived at by thinking about the symmetry of crystals, allowing the brothers to foresee the possibility of such polarization... . With experimental skill that was rare for their age, the young physicists investigated the new phenomenon completely, established the conditions of symmetry necessary to obtain it in a crystal, found the quantitative characteristics, which are surprisingly simple, and also measured the magnitude of the constants for several crystals." Somewhat later, the brothers also discovered the inverse piezoelectric effect, a phenomenon predicted by Lippman, and created a number of implements, including piezoelectric quartz and a biquartz plate.

Apparently, already in 1880, Pierre Curie was convinced that in order to realize the physical phenomenon it is necessary to remove the restrictions imposed by the conditions of symmetry of a material medium on the existence of the phenomenon: the phenomenon can exist only in a medium whose symmetry is compatible with the symmetry of the phenomenon. Indeed, the article entitled "On Symmetry" (1884) contains the first formulation of Curie's principle: "In order that the figure correctly portray the property at some point, it is necessary that it reveal the same elements of recurrence and symmetry, as the entire collection of actions produced by this property, or better said, as the entire collection of causes that give rise to the appearance of this property at the point being examined." (Ref. 1, p. 93).

Curie's principle as the symmetry aspect of the principle of causality was more completely formulated ten years later in the article "Symmetry in physical phenomena: symmetry of electric and magnetic fields" (Ref. 1, p. 111):

"It can also be seen that when superposing several phenomena of a different nature in the same system their dissymmetries add. Only those symmetry elements of the system remain that are common to each phenomenon taken separately."

"When certain causes produce certain actions, the symmetry elements of the causes must become evident in the actions produced.

"When certain actions manifest certain dissymmetry, this dissymmetry must also be manifested in the causes giving rise to them."

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These propositions are further illustrated with a number of examples: "Pyroelectric crystals of necessity have the symmetry of the subgroup of the electric field, since heating, assumed to be uniform, in itself does not contribute any dissymmetry. Piezoelectric crystals are more numerous than pyroelectric crystals: ... they include all the latter, and, in addition, they include crystals whose symmetry becomes less than the symmetry of the electric field only under the action of mechanical forces."

It may be noted that the permissible symmetry of piezoelectric crystals is defined here more precisely than in the article of 1880.

Besides formulating the symmetry aspect of the causality principle, Pierre Curie also obtained a number of other remarkable results in the theory of symmetry. With complete justification, we can say that Pierre Curie predicted the idea of color symmetry (contained in his concept of the symmetry of a material medium) and of gauge transformations of the equations of physical effects (method of renormalization group). Limiting symmetry groups, derived by Curie, permitted constructing a classification of oriented tensor quantities according to the symmetry type. The principle of symmetry used by Curie for making predictions, searching and studying piezoelectric and magnetoelectric effects, is widely used for the same purposes in the generalized formulation in modern crystal physics.[3,4]

The discovery made by the Curie brothers gave powerful motivation to the vigorous development of the electrophysics of dielectrics observed today, and this note would be incomplete if we did not try to examine the basic stages of the subsequent development and present state of research and applications of piezoeletricity and of the properties of crystals related to it. According to our information, by 1980, piezoelectric properties were quantitatively measured in 385 structures, pyroelectric properties in 98, ferroelectric in 405, linear electro-optical in 189, and nonlinear optical in 98.[5-7]

Without dwelling on the early stage of the development of scientific and applied research in this area, connected with the names of Langevin, Cady, Nicholson, Debye, Sears, Bikar, Luke, Sokolov, and other scientists, we will briefly describe the most important of the existing and potential applications of dielectric crystals without a center of symmetry. Historically, piezoelectric applications were the earliest. The oldest of the piezoelectrics, single crystal piezoelectric quartz, continues to dominate frequency stabilization in diverse radio electronic devices, ranging from common watches to precision filters for volume and surface acoustic waves. The main piezoelectric materials, judging from the production volume, used in ultrasonic and electroacoustical (including hydroacoustical) devices, are different forms of polarized ferroceramic, primarily based on zirconate-lead titanate with the perovskite structure, manufactured in quantities of thousands of tons and millions of objects such as radio parts and components: capacitors, resistors, piezoelectric transformers, posistors, variable capacitors, and many others.

Pyroelectric properties, first discovered a long time ago, have today created the basis for the development and application of a wide spectrum of devices, which yield the most interesting results in such diverse fields as infrared photography from space, medical diagnostics, protection of objects, and technological monitoring.

The main materials used in electrooptical devices for amplitude and phase modulation, as well as for deflecting laser beams, are single crystals of the calcium dihydrophosphate family (KDP-DKDP, ADP, CDA, DCDA) lithium niobate and tantalate, and germano- and silicosillinite.

The strong optical nonlinearity of such noncentrosymmetric crystals, such as lithium niobate and iodate, together with the high beam strength of KDP type crystals, has led to the creation of modern nonlinear optical frequency converters, second, third, and fourth harmonic generators of garnet and neodymium glass lasers, as well as parametric generation of light and visualization of infrared radiation by upward frequency conversion.

In conclusion, let us evaluate the degree of prominence of acentric structures with the special properties of interest to us. The average statistical weight of acentric structures in the overall number of substances, determined to within the point group, exceeds 30%. At the present time, more than two million individual substances are known, including about three thousand minerals and more than 40 thousand inorganic and complex compounds (the remaining substances are organic and bioorganic compounds and biopolymers). The possible number of acentric structures exceeds 600 thousand, of which, as indicated above, special properties have been identified in approximately two thousand, approximately 600 have been measured, and not more than 50 dielectrics are used.

The comments made above illustrate the enormity of the field of forthcoming research in the upcoming second century of the study of properties related to piezoelectricity, connected with acentric properties of crystal structures. Based on the fact that the overwhelming majority of acentric structures are dielectrics, we are justified in asserting that the day is close when the dielectronics stage, which follows after the vacuum and semiconducting electronics stages, will enter into electronic technology without terminating the earlier stages, but supplementing and coexisting with them.

We conclude our brief historical sketch with the words of Joliot-Curie (cited in Ref. 2, p. 106): "In order to evaluate the path taken by science, the example of Pierre Curie ..., who completed many works, each of which could make any scientist famous, the discovery of piezoelectricity, the discovery of laws of symmetry in physical phenomena and the basic laws of magnetism, and finally, together with Marie Curie the discovery of radioactive elements, is characteristic."

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