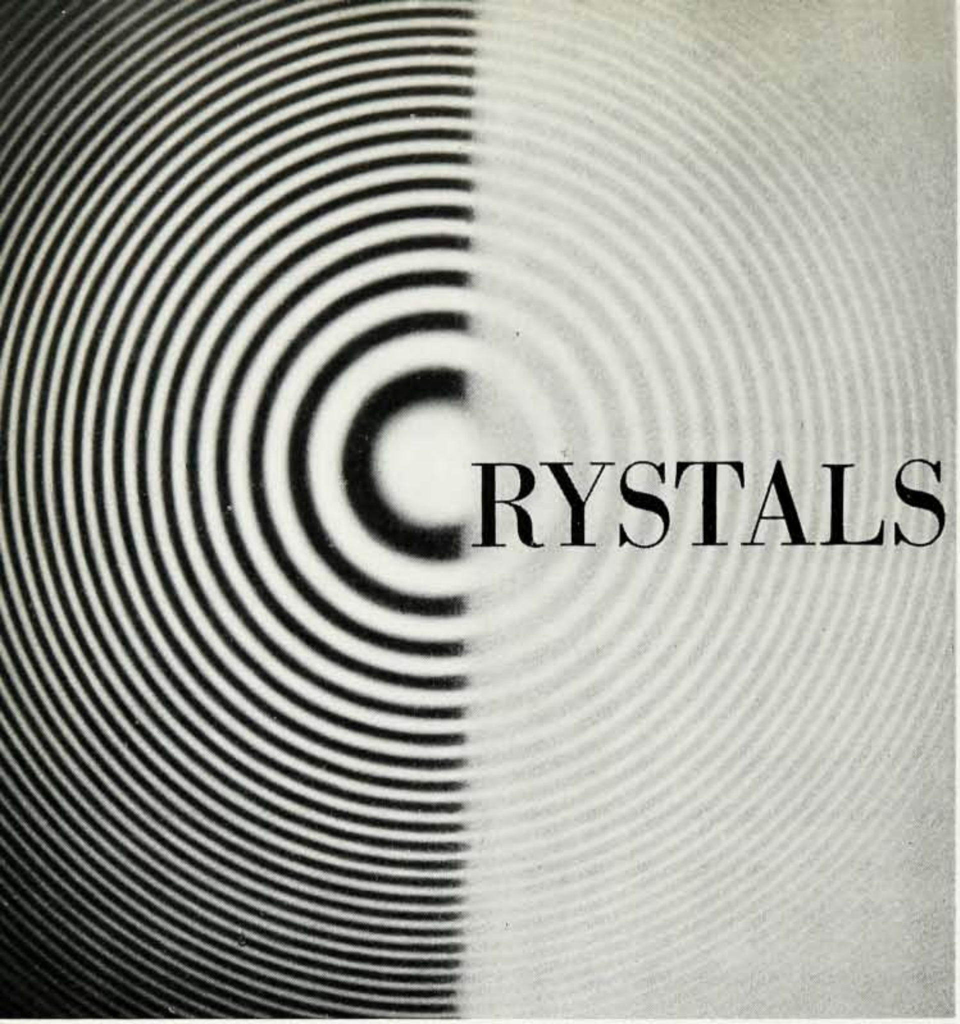

The Polaroid Corporation

CRYSTALS

by ***Hans Jaffe***

The demand for single crystals has outstripped nature's bounty. Research in crystal physics has revealed the opportunity for breeding new species which are better adapted than natural crystals to many technical applications.

In times past, well developed clear crystals were a rare gift of nature and were highly valued. Their luster and regularity of shape have been a source of pleasure to the layman through the centuries and a cause for speculation to the naturalist and philosopher.

Actually, most solid substances we meet in everyday life are crystalline, as recent progress in physics and chemistry, and investigation by x-rays in particular, have shown. All metals are crystalline, for example, and so are building materials such as brick and even clay. Thus, while the study of the crystalline state flourished because it proved fundamental to our whole knowledge of the structure of materials, the role of single crystals seemed diminished by the progress of technology which could provide ground glass jewels to take the place of many a natural stone. The mineralogist's cabinet was relegated to a less important corner of the science building in our universities while physics and chemistry spread.

There is, however, no field of science which will not sooner or later be called upon to play its own particular role in the development of modern industry. The last twenty years have seen a revival of interest in large uniform crystals such as nature provides only in rare cases and a whole industry has sprung up to produce such large crystals to supplement the scarce supplies of nature or to provide combinations of properties not found at all in natural crystals. The ability of some crystals to translate mechanical into electrical energy (and vice versa) is vital to modern communication technology.

Crystals in Science and Industry

Large uniform crystals are being used for two general purposes. The first is based on the greater uniformity and strength which a single large crystal or section of a crystal may have compared to a piece of common matter consisting of a great many tiny interlaced crystals. Here belongs the use of artificial sapphire crystals for watch and instrument bearings and for phonograph needles, and the use of mica for insulators in electron tubes and the like. The greater transparency and clarity of single crystals as compared to multi-crystal masses led to the use of prisms and lenses made of artificial crystals of sodium chloride, lithium fluoride, and other salt type crystals in spectrographs operating far into the infrared and ultraviolet regions of light. Crystals, free to an extreme degree of thermal disturbances or irregularities, are needed in crystal ionization counters for measurement of nuclear radiation. Fluorescent crystals, such as anthracene and calcium tungstate, serve the same purpose in scintillation counters.

The second kind of application is based on a fundamental property of single crystals—their dependence on direction in responding to various physical agents. This directionality is a consequence of the arrangement of matter in a uniform array of a large number of identical unit cells—the manner of array varying for different crystals.

The best known manifestation of a crystal's directionality is birefringence or double refraction—the splitting of a beam of light into two rays as it passes through a crystal. It was this phenomenon in crystals which led to the discovery of polarized light some two hundred years ago and which made crystal optics one of the most interesting but also most difficult fields of physics as it was studied in the nineteenth century.

The brilliant development of the plastic sheet polarizer known as "Polaroid" seemed at first to banish the crystal from the field of applied polarized light; but here is another case where a new development, rather than making other materials obsolete, gave them eventually an increased field of application. There are certain applications of polarized light such as for a wide-field ring sight for anti-aircraft guns (and maybe your own shotgun) which depend on a combination of Polaroid and polarizing crystals. This application, impossible without Polaroid, has probably used a greater quantity of crystal material than all polarizing devices used in the first world war when Polaroid was not available.

Piezoelectricity

The most important application of single crystals today is that of piezoelectric—literally "squeeze-electric"—devices. The piezoelectric effect is the relation between a mechanical deformation of a crystal element and an electric charge appearing on its surfaces. The effect works both ways. You may charge a crystal with a battery or with an amplifier's output and obtain a slight stretching or twisting of the crystal element which may be used to drive the diaphragm of an earphone or the like; or you may deform the crystal by a mechanical force, by a sound wave for instance, and obtain a charge on the crystal surface which may be fed to the grid of a vacuum tube.

The essential advantages of this piezoelectric action are the simplicity, the high stiffness, and small weight of the crystal slabs or elements in which this action takes place. This makes it possible to use the element up to very high frequencies. A characteristic of piezoelectric devices, compared to other means for translating electrical to mechanical energy and vice versa, is the high electrical impedance and the rather high voltage involved in the piezoelectric action. This characteristic makes the piezoelectric crystal

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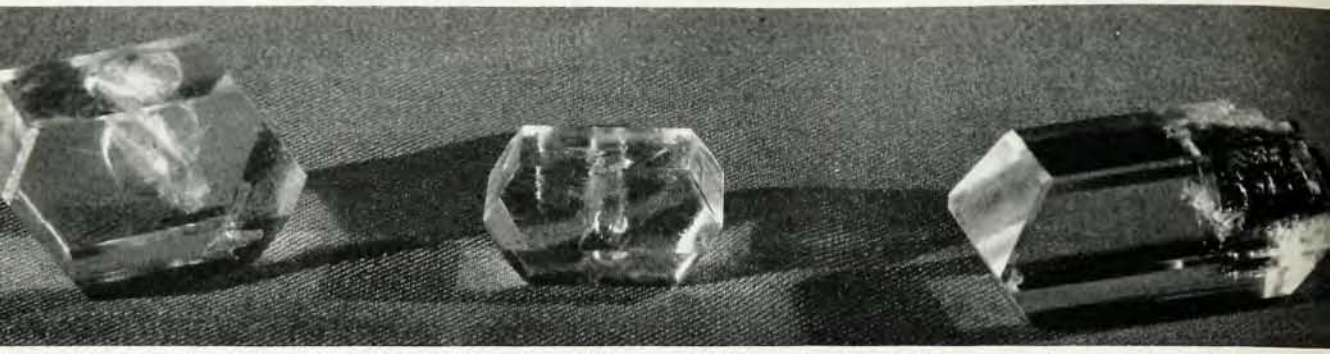

Lithium sulfate monohydrate crystals
The Brush Development Company

ideal in combination with vacuum tubes. It is thus no coincidence that the large-scale development of piezoelectricity does not date from the time of its discovery, which took place in 1880, but followed the development of the vacuum tube around 1920.

The particular quality of a crystal required for piezoelectricity is the absence of a center of symmetry. Certain directions in the crystal must be polar; the aspect of the motif of the unit cell must be different whether you pass through the crystal from right to left or left to right. A coarse example of a body without center of symmetry is a stack of typewriter paper interleaved with carbon paper. The polarity of the stack becomes apparent if one puts it into a typewriter the wrong way.

Of all investigated crystals, only ten to twenty percent fulfill the condition of asymmetry which is necessary for piezoelectricity. The majority of crystals, among them the best known such as rock salt, calcite, and alum, have a center of symmetry and therefore are not piezoelectric at all. Of those crystals which show the required lack of symmetry, the majority have a piezoelectric effect which is too small for technical use and among mineral crystals only two, quartz and tourmaline, have found practical application.

Industrial development of synthetic piezoelectric crystals until quite recently was limited to one substance, Rochelle salt. It is interesting to note that these three substances were among the first crystals to be studied by the discoverers of piezoelectricity, the brothers Jacques and Pierre Curie, back in 1880. The only practical application of the new effect made by its discoverers was in an electrometer using the small deformation of a quartz strip as a means of measuring a high electric voltage. This instrument was used by Pierre Curie and Marie Curie in their studies of the ionization of air by radioactive substances.

Quartz and Rochelle Salt

Quartz has maintained an eminent position in the laboratory and in many technical applications. This is not so much due to the magnitude of its piezoelectric effect—which indeed is rather low—but to a combination of several highly desirable properties. Among these are high stability against chemical attack and heat, and great mechanical toughness. The remarkably elastic behavior of quartz permits one to cut plates that will maintain their resonance frequency within extremely narrow limits even under considerable variations of temperature. These characteristics of stability have led to the widespread use of quartz crystals to control the frequency of radio transmitting and receiving equipment.

Many millions of dollars were spent during the war for quartz plates to control the frequency of military communication equipment. The essence of this use of a crystal for frequency control is the maintainance of the electric oscillations of the circuit at the mechanical resonance frequency of the crystal. We are all familiar with the constancy of pitch and persistence of sound of mechanical systems such as bells or tuning forks. By comparison, persistence and stability of oscillation of an electric circuit is quite limited due to the electric resistance and variability of inductance present even in the best tuning coils. If a crystal is inserted properly into an electric oscillating circuit, this crystal will be made to vibrate at its characteristic mechanical frequency by the energy of the electric circuit and in turn will force the electric circuit to adjust its oscillation to the crystal frequency. Thus in a crystal oscillator the electric signal is first transformed into a mechanical signal and then back into an electrical signal by means of piezoelectricity.

In its original application, the transformation of mechanical into electrical energy and vice versa, the small piezoelectric effect of quartz is a severe drawback and it is in this field that synthetic crystals have seen an important development. Leading in the field is Rochelle salt, which is a compound of tartaric acid made from winery residues. This substance was one of the compounds on which Pasteur made his famous investigations relating the asymmetry of chemical substances and of the crystals which they form. Indications of an unusually high piezoelectric effect were obtained by Pockels in Germany as early as 1893.

Practical interest in this crystal dates from the days of the first world war. Langevin in France showed at that time that quartz crystals could be used to produce and detect ultrasonic waves under water. Following this, several American investigators undertook work on Rochelle salt, among them Cady at Wesleyan University working on a Naval research program, and Nicolson at the Western Electric Company. The latter developed a variety of devices for generating and picking up audible sound waves in air.

Devices built by these early investigators were erratic in their behavior. This was due to imperfection of the crystals as well as an incomplete knowledge of the physical properties of the substance. The following decade brought the development of industrial crystal growing and fabrication by Sawyer and Kjellgren at the Brush Laboratories and the Brush Development Company which assured a supply of uniform Rochelle salt crystal material and crystal elements.

The outstanding property of Rochelle salt is the exceptionally high value of its piezoelectric modulus, which is a measure of the mechanical motion obtained per unit applied voltage; with it goes a high dielectric constant, well above one hundred. Under typical operating conditions, a suitably cut Rochelle salt strip one inch long and one-twentieth inch thick will expand twenty millionths of an inch if one hundred volts are applied. This would appear to be a very minute motion but is over one hundred times as much as obtained from a quartz strip of the same size and shape. A stepup by a factor of ten to fifty, depending on the ratio of length to thickness, is obtained by a multiplate construction which transforms the expansion and contraction of two opposing crystal strips into a bending or twisting motion.

As an electric generator, a single Rochelle salt strip one inch long, one-half inch wide, and one-twentieth thick, produces an electromotive force of thirty volts when a force of one pound is applied to its end faces. The corresponding short-circuit current, in microamperes, is, numerically, about one-tenth the frequency of the applied mechanical signal. Quartz would give about half the voltage but only one two-hundredth the current. High voltage output, high capacitance, light weight, and independence from stray magnetic fields make Rochelle salt elements eminently suited for microphones and phonograph pickups. You will find one in the pickup cartridge of the great majority of all phonographs now in American homes.

New Synthetic Crystals

For applications involving high power handling capacity, or operation under extreme climatic conditions, Rochelle salt is limited by chemical instability over fifty-six degrees centigrade. Systematic investigations of other piezoelectric crystals were therefore undertaken beginning about ten years ago and numerous crystal species were grown and measured. Most were found to have too low piezoelectric moduli, others were not stable at high tem-

Rochelle salt crystals ready for machining
The Brush Development Company

An ammonium dihydrogen phosphate (ADP) crystal grown from a large seed plate and small ADP crystals which grew spontaneously in the same solution; the latter are twins.
The Brush Development Company

peratures or had undesirable mechanical properties.

Success came with ammonium dihydrogen phosphate (ADP), a crystal with good mechanical properties, stable to one hundred and forty degrees centigrade, and showing a piezoelectric modulus roughly midway between quartz and Rochelle salt. This modulus is highly adequate for the use of the ADP crystal as a driver in the ultrasonic frequency range where even a small amplitude of motion corresponds to a high level of radiated energy. In particular, this is true when the crystal is made to radiate sound energy into a liquid.

Fortunately, the Brush Development Company had carried study and development of this crystal to the pilot production stage when, in 1942, the need for a husky crystal to generate ultrasonic waves became very urgent. A cooperative effort under Naval sponsorship led to large-scale production in a very short time.

As an acoustic driver operating in air at audible frequencies, the ADP crystal requires high voltages which at present are impractical. However, in electromotive force generated per unit applied pressure (given by the modulus divided by the dielectric constant) the ADP crystal is about twice as good as the common cut of Rochelle salt. This makes the ADP crystal suitable for voltage-generating devices working into a high impedance such as hearing-aid microphones or phonograph pickups.

For work with ultrasonic waves of high frequencies (from one megacycle up to twenty megacycles and more) quartz still occupies an important place. Another synthetic crystal, lithium sulfate monohydrate, competes with quartz for this frequency range; but for the maintenance of frequency to high standards of accuracy, quartz crystal oscillators are unchallenged today. No other crystal is in sight to replace quartz for these critical applications.

In less exacting applications of controlled frequency the possibilities of quartz are not fully utilized and other crystals synthetically produced can replace quartz if economic circumstances warrant. This is true in particular when crystals are used for electric filter and frequency discrimination purposes. As the size of a crystal is roughly inverse to the frequency to be controlled, quartz crystals used for filters at fairly low frequency are of considerable size.

Such filters are needed in multi-channel telephone circuits. Systematic measurements of piezoelectric and frequency characteristics were carried out at the Bell Telephone Laboratories. ADP and several other crystals were found quite suitable, except for one decisive factor: the resonant frequency varied too much with temperature. Satisfactory independence of temperature was found in a purely organic crystal, ethylene diamine tartrate (EDT). Very few years after its discovery as a new piezoelectric crystal, this material is now in use in the American telephone system. Neutral potassium tartrate crystals, now also available, have similar and in some respects superior characteristics.

Crystal Light Valves

An interesting phenomenon peculiar to piezoelectric crystals is the linear electro-optic effect, that is an influence of an applied voltage on the transmission of polarized light. This effect may be applied in various devices involving modulation of a light beam, and offers many advantages over the quadratic Kerr effect in liquids.

The ADP crystal and certain chemically similar crystals show definite promise for light modulator applications in sound recording and television. Zinc blende (zinc sulfide) is a crystal with a rather weak piezoelectric effect but promising electro-optic properties. Unfortunately, no sufficiently perfect zinc blende crystals have been obtained either in nature or the laboratory thus far.

Crystal Growing

Discovery of desirable piezoelectric or other physical properties of a substance not found in nature is only the first step towards introduction of the material on a technical scale. Methods of producing these crystals in large and flawless pieces of uniform structure and orientation must be developed.

Piezoelectric crystals on a technical scale at present are grown exclusively from solutions, usually in water. Generally speaking, a high purity of the solution is needed, but in certain cases it has been found that small amounts of specific materials added to the solution help the crystals to grow into the desired shapes and sizes. Rochelle salt and ADP are grown by very slow cooling of their saturated solutions. A circulation method involving three tanks at different temperatures is used by the Bell System for the production of the EDT crystal.

Some crystals for optic application are grown from the molten state by slow freezing, for instance sodium chloride, lithium fluoride, and silver chloride. This process of growing crystals from the melt has been developed by various university laboratories, including the Massachusetts Institute of Technology, and is now being carried out on a production scale by the Harshaw Chemical Company. Sodium nitrate, a good crystal for polarized light devices, may be grown either from a solution or from the molten state.

In all methods of growing crystals a decisive factor is the starting point of crystallization or provision of a suitable seed crystal. For growth from solution a seed body of chosen shape and orientation is introduced and growth is induced by change of temperature or evaporation of the solvent. When growing from the melt, a start of crystallization at the desired point may be procured by suitable shape of crucible or oven. An interesting alternative by the Polaroid Corporation is the introduction of a large body of a similarly formed foreign crystal into the melt which serves as a basis for crystallization.

With considerable success achieved in growing crystals of substances not found crystallized in nature, we are tempted to reproduce nature's work in providing large amounts of mineral crystals such as quartz, tourmaline, and calcite by crystallization in the laboratory. Promising results have been obtained already. Ersatz-minded Germans during the late war worked hard to grow crystals of quartz and mica, the former for piezoelectric applications, and the latter for various insulation jobs. Since then these projects have been pursued vigorously in this country. Growth of quartz is being studied in several laboratories. Readers may judge success from photographs.

Special methods have been developed in Switzerland and later refined in this country by Linde Air Products and others for the production of corundum (synthetic ruby) for bearings, gages, and jewel purposes. The melting point of this substance is so high (above two thousand degrees centigrade) that cooling of a melt in a crucible is not a practical way of obtaining homogeneous crystals. The actual method depends on blowing extremely fine powdered material through a flame. The fine particles melt in the flame and are then deposited upon a seed crystal. Spinel, titanium dioxide, and calcium tungstate crystals have recently been made by this method. Thin but extended crystal sheets of cadmium sulfide are grown by reacting cadmium vapor with hydrogen sulfide gas.

In spite of much recent development, crystal growth is a slow process. The development of Polaroid has shown that optical properties typical of single crystals can be imparted to noncrystalline substances. Is this true also of the directional character responsible for piezoelectricity? The affirmative answer is indicated by the electret (Physics Today, March 1949) and by the important piezoelectric properties shown by the polycrystalline ceramic, barium titanate, after polarization with a high voltage. Barium titanate is the electric analogue to ferromagnetic materials; indeed, a permanent magnet has polarity much like a piezoelectric crystal. But this is another story—meanwhile, any suggestions on how to grow an egg-sized diamond?