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PIEZOELECTRICITY OF CRYSTAL QUARTZ

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Abstract

Piezoelectricity of crystal quartz at constant temperature.—Experimental measurements with the quadrant electrometer of the distribution of the piezoelectric charge over the surface of a quartz crystal in a plane normal to the optic axis were found to vary in such a manner as to produce six regions of charge, three positive areas alternating with three negative. The areas had definite geometrical relations to the electric axes and therefore these facts yielded a new and accurate method of determining the directions of the electric axes in crystal quartz. In planes containing the optic axis there was a region of positive charge separated by a line in the direction of the optic axis from a region of negative charge.

Variation with temperature of the piezoelectric effect in quartz.—The piezoelectric effect increased by 20 percent from room temperature to 60°C and decreased thereafter, reaching zero at about 573°C. Cooling curves showed a lag.

Variability of the piezoelectric effect.—The piezoelectric charge produced on different specimens or on different areas of the same specimen, all specimens being optically perfect, varied from large positive values of charge to large negative values. In general, the surface of the crystal quartz produced piezoelectric charges of the same sign, but of varying magnitudes. The charge measured over the entire surface of a crystal appeared to be the average of the effects of the elementary areas. The specimens in the present experiments varied on the negative side of the crystal from 5.8×10^{-8} to 7.1×10^{-8} e.s.u./cm$^2\times$dyne, while on the positive side the variation was from 4.9×10^{-8} to 6.4×10^{-8} e.s.u./cm$^2\times$dyne. These numbers are not far from the accepted value of 6.3×10^{-8} e.s.u./cm$^2\times$dyne, of the "piezoelectric constant" of P. and J. Curie. Such variations are in keeping with recent x-ray investigations on the imperfections of crystals which indicate that crystals are mosaics of an elementary perfect struture.

Introduction

An investigation perhaps more extensive than has been hitherto attempted of the piezoelectric effect in crystalline quartz is described in the following pages. The experiments have been greatly facilitated by exceptional opportunities existing in this laboratory for the selection and cutting of samples of quartz. The general laws of piezoelectric action, already well established, have been corroborated in full but in addition many new and unsuspected facts have been discovered. The theory of the piezoelectric effect available at present, although adequate for a description of the more general laws, is apparently incapable of coping successfully with the new phenomena. It appears that the formulation of a complete theory must await a more comprehensive understanding of the molecular structure of quartz. Further, the piezoelectric effect at various temperatures has been measured.

At the outset we may call to mind that a crystal of quartz is in the form of a hexagonal cylinder surmounted by a hexagonal pyramid; the faces of the crystal, which may vary in length and breadth, lie at definite angles with each other. In Fig. 1, *JEGK*, *GDLK*, *DLMF*, *MNHF*, *HNIC* and *CIJE* are the sides of the hexagonal cylinder, the angle between any two adjacent sides is 120°. The faces of the hexagonal pyramid *JKLMNIA* lie at an angle of 38°13′ to the faces of the cylinder. The quartz crystal, a section of which is shown in Fig. 1, has four axes of symmetry namely, *AB*, *CD*, *EF* and *GH*. *AB* is called, in crystallographic terms, the trigonal axis, as there exists three symmetrical positions of the crystal as it is rotated about this axis. *AB* is also called the optic axis, because along this direction the crystal has unique optical properties. *CD*, *EF* and *GH* are digonal exes of symmetry, for there are only two positions of symmetry as the crystal is rotated around each of these axes. *CD*, *EF* and *GH* are known as the electric axes, since a pressure applied to the crystal parallel to these directions produces piezoelectric polarization in the same direction.

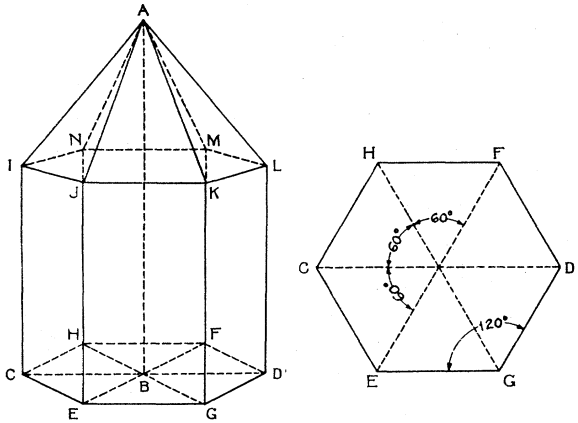

Fig. 1. A section of a quartz crystal showing the direction of the optic and electric axes.

No complete historical summary of the many researches on the piezoelectric phenomenon will be attempted here, but some of the more important papers may be mentioned. We pass over the early qualitative experiments of W. C. Roentgen[1] and direct attention to the more quantitative investigations of P. and J. Curie[2] in which were first brought out the laws governing the piezoelectric effect in quartz. Their studies made on a rectangular parallelopiped of quartz cut in such a manner that one of the electric axes was perpendicular to one of the faces, led them to conclude that a force applied along the electric axis produced a charge on the faces perpendicular to this axis that was directly proportional to the force, a positive charge accumulating on one of the faces and an equal negative charge on the opposite face. A reversal of the sign of the force produced a reversal of the charges. The magnitude K of the charge, was found to be 6.32×10^{-8} esu/dyne cm^2. This has been the accepted value. The present investigation shows that this

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[1] Roentgen, Ann. d. Physik und Chemie, NF**19–20**, 513 (1883).

[2] P. and J. Curie, Comptes rendus **91**, 294 (1880).

value is not a constant for all quartz but varies very materially for different specimens of optically perfect quartz. This is in keeping with the general ideas of crystal imperfections as discussed later.

W. Voigt[3] has developed theoretical formulas for the piezoelectric charges in terms of the piezoelectric and elastic constants of the quartz. His formulas agreed with the experimental results of P. and J. Curies and from their piezoelectric constant he was able to deduce the various piezoelectric constants of the equations for quartz.

Recently W. Bragg[4] and R. E. Gibbs[5], from their x-ray studies of the molecular structure of crystal quartz have explained the piezo-electric effect as a distortion of the uniaxial nature of the crystal; while the production of pyroelectricity is due to the change of structure towards or away from hexagonal symmetry.

Experimental Details

The apparatus shown in Fig. 2 consisted of a Compton electrometer *A* with a sensitivity of about 0.004 V/mm suitably shielded by an earthed brass cylinder *B*. The quartz *C*, under investigation, was placed upon the circular platform *D*. This platform was fixed in a horizontal position in such a manner that it could be rotated about the vertical axis *G* and the amount of rotation measured by the circular scale *E*. A longitudinal motion could be given the platform *D* by the screw *K* and measured by the divided head *L*. Thus any point of the quartz could be brought under the copper contact point *M*. The contact point was connected to the electrometer and insulated throughout by fused quartz. The apparatus was thoroughly shielded electrically and properly insulated switches were placed in the system. In some of the experiments, it was found desirable to apply or release the pressure on the quartz in a direction parallel to the plane of the

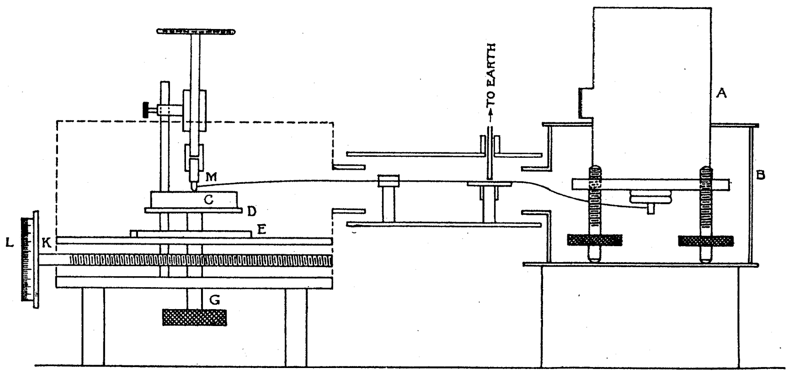

Fig. 2. Apparatus for the investigation of the piezoelectricity of quartz.

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[3] Voigt, Ann. d. Physik u. Chemie, NF55, 701 (1895).

[4] Bragg and Gibbs, Proc. of Roy. Soc. **A109**, 405 (1926).

[5] Gibbs, Proc. of Roy. Soc. **A110**, 443 (1926).

platform *D*. To accomplish this an instrument was designed in which a quick application or release of pressure to the contact point could be made by a suitably actuated cam.

In order to raise the quartz to any desired temperature an electric resistance furnace with a metal core was constructed which could be placed over the quartz and the core earthed, thus shielding effectually the quartz and contact point. To measure the temperature a calibrated chromel-nichrome thermocouple was inserted in the furnace with the quartz.

The capacity of the system which varied during the investigation from 34 m.m.f. to 41 m.m.f. was compared with the capacity of a standard condenser by the heterodyne beat method, the measurements being reliable to less than one percent.

Piezoelectric Effects in the Direction of Pressure

Experiments were undertaken to determine the character of the distribution of charge over the surface upon which the pressure was applied. Specimens of optically perfect quartz were selected and cut in such a manner that the electric axis was normal to the large face of a parallelopiped $25\times28\times1$ mm. Each crystal was placed on table *D*, Fig. 2, and explored over the largest faces by releasing 1000 grams pressure from the contact point which had an area of about 0.1 mm^2.

In general one side of the crystal would give positive deflections while the opposite side gave negative deflections. Small areas of negative charge were often found on the faces which gave positive deflections over most of the face; and corresponding areas of positive deflection were found on the negative face. Large deflections might occur at the center of the quartz or at the edge and the deflection for one crystal was often twice that of another crystal. There seemed to be no uniformity of results.

The question arose whether such a distribution was of permanent character. To answer this a crystal was subjected to a force of about 25 kilograms for 20 seconds and the surface explored and no change in the distribution could be observed. The same crystal was then raised to a temperature of approximately 600°C, thus transforming it to the Beta-quartz. After allowing it to return to the alpha-quartz state, the surface was again explored. Again no change was observed. Thus the distribution seems to be permanent.

To substantiate further the above results, a piece of quartz cut in the above manner and about $150\times100\times3$ mm was subjected to the exploring test and again the charge was found to vary over the surface. The piece was then cut into three parts and each part explored, but no change could be observed in the character of the distribution of the original charge. Each part was examined optically and observed to be free from twinning and other defects.

These variations in the piezoelectric charge are naturally to be attributed to imperfections in the quartz crystal, although these imperfections may be so minute as to escape detection by the usual examination with polarized light. All that can be said is that the imperfections might be in the nature of small crystal fragments variously oriented in perhaps a random manner with respect to the large parent crystal, and that these little fragments are small in size, say less than 0.1 mm in their largest dimension. It may be pointed out further than these imperfections may be very small, indeed such as would result from a displacement of a small group of molecules. Recent developments in x-ray analysis of crystals lead to the idea that crystals are not perfectly formed as hitherto supposed[6,7,8], but are constituted of a mosaic of more elementary perfect structures, and that the axes of the more perfect crystals are not oriented in the same direction but may vary from a mean position. This explanation may account for the peculiar variation of the piezoelectric charge over the surface of quartz, although surface or volume strains may be contributing factors.

Distributions of Charge Around the Cylindrical Surface of a Circular Piece of Quartz Cut Perpendicular to the Electric Axis

A cylindrical specimen of quartz 60 mm in diameter and 30 mm thick was cut from a rough piece of quartz free from flaws and twinning, in such a manner that an electric axis was normal to the ends of the cylinder and the optic axis parallel to the plane of the ends, the other electric axes being as shown in Fig. 3. An exploration of the distribution of the charge over the cylindrical surface was carried out by the application of a weight of 1000 gms directly to the exploring point which was placed perpendicular to the surface of the quartz. Care was taken to fasten the quartz cylinder concentrically on

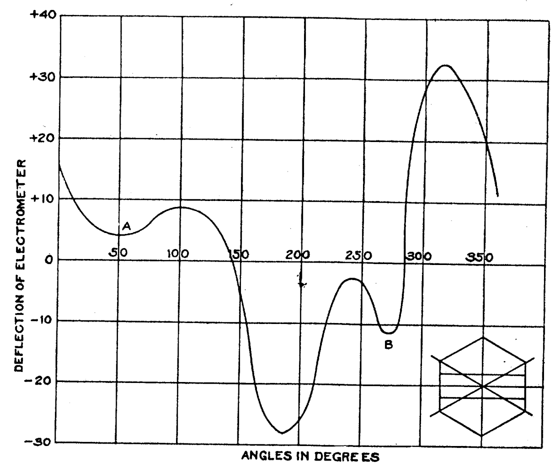

Fig. 3. Distribution of piezoelectric charge over the cylindrical surface of a crystal of quartz in which the plane containing the optic axis and the line perpendicular to one of the hexagonal sides of the crystal is parallel to the ends of the cylinder.

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[6] W. L. Bragg, Darwin and James, Phil. Mag. **1**, 897 (1926).

[7] A. Muller, Nature, 121 (May 22, 1926).

[8] Burgess, Nature, 116 (July 24, 1926).

table D, Fig. 2 and to have points of reference marked on it in such a manner that the data could always be referred back to the original sepcimen. The character of the distribution is shown in Fig. 3 where the abscissas are the angles of rotation of the quartz which were read every degree and the ordinates are electrometer deflections.

There appears to be one well defined region of positive charge and another of negative charge, the magnitude of the deflections of each being about equal, but the area of the positive region is larger than that of the negative.

One peculiarity which seems to be characteristic of the curve is the decrease of the curve to a minimum at A and then a rise to a maximum and finally a decrease to zero in the positive area and a similar phenomenon taking place in the region of point B in the negative area. It may be mentioned that the general characteristics of the curve always remained the same regardless of the method of holding the specimen to the plate.

Distribution of Charge Around the Surface of a Cylindrical Piece of Quartz in Which Two Electric Axes Lie at 60° to the End Faces

Next a cylindrical crystal of the same dimensions but cut as indicated in Fig. 4 was placed concentrically on table D. The results of a procedure similar to the previous case is shown in Fig. 4 and it can be seen that there are two well defined regions, one of the positive charge and the other negative. The maximum deflections in both the positive and negative regions are of the same magnitude, but appear to occur about 150° apart and not 180°. The direction of the line dividing these areas lies more or less in the direction of the optic axis.

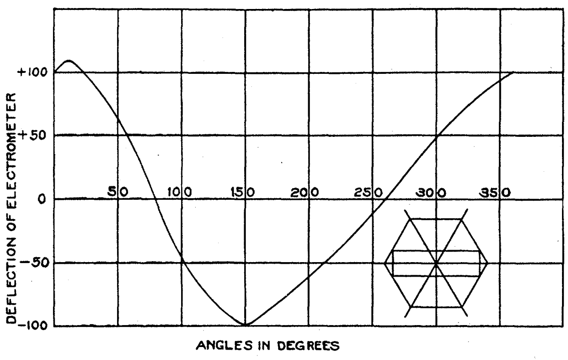

Fig. 4. Distribution of piexoelectric charge over the cylindrical surface of a crystal of quartz in which the plane containing the optic and an electric axis is parallel to the ends of the cylinder.

Distribution of Charge Over the Cylindrical Surface of a Crystal in which the Optic Axis is Perpendicular to the Ends of the Cylinder

Finally, a crystal of the same dimensions as in the two previous cases was cut from a rough crystal in such a manner that the optic axis was normal to the ends of the cylinder. The exploration of the cylindrical surface was carried out in a manner similar to the two preceeding cases, and the character of distribution of the charge is shown in Fig. 5. There are three positive maxima and three negative and they occur accurately 60° apart and are the same magnitude and alternate in sign. There are six points where the charge becomes zero and they lie 60° apart.

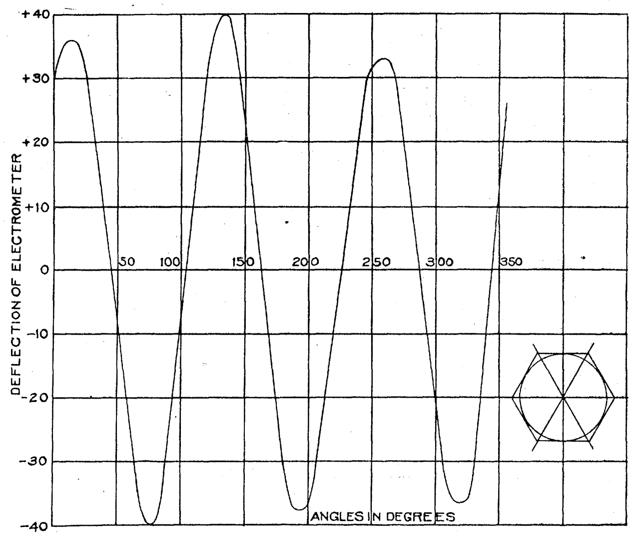

Fig. 5. Distribution of piezoelectric charge over the cylindrical surface of a quartz crystal in which the ends of the cylinder are parallel to the plane of the electric axes.

A METHOD FOR DETERMINING THE ELECTRIC AXES OF A SLAB OF QUARTZ CUT IN SUCH A MANNER THAT THE OPTIC AXIS IS PERPENDICULAR TO ITS PLANE

The above experiment serves as a new and precise method for determining the direction of the electric axes of a piece of quartz cut normal to the optic axis and in which there are no indications of the crystal form. The rough piece of quartz must first be examined for the optic axis and then cut into slabs of the desired thickness in which the optic axis is normal to the plane of the slab. The slab in which the directions of the electric axes are to be determined is placed on table *D* Fig. 2 and an exploration of a cylindrical surface, more or less parallel to the optic axis, is carried out and the points of either maximum or minimum deflection observed. In most cases the latter is preferable as being more accurately determined. In case two diametrically opposite points can be determined, it is only necessary to draw a line joining them, but in case of the absence of the opposite point the lines must be drawn in the direction of pressure. Now it must be remembered that the direction of production of zero charge lies normal to the electric axis of the piece; therefore it is only necessary to draw lines perpendicular to the observed lines to locate the electric axis.

In many cases that may arise it is impossible to find a surface on the quartz which will be nearly normal to the direction of pressure; then it is possible to produce such a surface by grinding a semi-cylindrical notch in the side of the quartz in such a manner that the generator of the semi-cylindrical surface is parallel to the optic axis. Thus placing the quartz on the table D in such a manner that the center of the notch coincides with the center of rotation of the table the exploring point can be brought in normal contact with this surface.

Many trials were made with this procedure both on samples of quartz in which faces were present and others in which faces were absent. In either case the electric axis could easily be determined within 2°.

Measurement of the Magnitude of the Piezoelectric Effect

Samples of quartz 28×25×2 mm and 28×25×1 mm were cut with an electric axis normal to the 28×25 side and the two faces in contact with the electrodes parallel to each other within .025 mm. Forces of 50, 100, 200, 500, 1000 and 2000 grams were applied to each in the direction of the electric axis and in such a manner as to be equally distributed over the entire surface of the crystal. It was found after a few experiments that more consistent results could be obtained by sputtering the surfaces of the quartz in contact with the electrodes with platinum. Four samples of the results obtained are given in Table I and are representative of the results obtained in many trials on different crystals.

Table I

Crystal Number	Dimension in mm of surface in contact with electrodes	Charge (esu/cm^2 dyne) $\times 10^8$	Date	Temp. °C
1 (a)	27×25	(−6.27 ± .23)	June 10	19.5
(b)	27×11.5	(−6.37 ± .11)	" 24	24
(c)	16×12	(−7.18 ± .16)	" 28	24
(d)	11×8.5	(−6.89 ± .10)	" 28	24
(e)	12×12	(−7.11 ± .16)	July 1	21
(f)	11.5×12.5	(−6.43 ± .18)	" 1	21
2 (a)	27×25	(−6.05 ± .15)	June 11	19.5
(b)	27×25	(−5.88 ± .12)	" 16	21
(c)	27×25	(−6.16 ± .16)	" 17	19.5
(d)	27×25	(−6.42 ± .30)	" 17	19.5
(e)	27×25	(+4.94 ± .40)	" 17	19.2
(f)	27×25	(+5.38 ± .04)	" 19	19.0
(g)	27×25	(+5.47 ± .26)	" 21	19.0
3	27×25	(+4.99 ± .04)	June 28	24
4	27×25	(+6.41 ± .05)	June 28	24

Crystal number 1 was first explored by the point method and it was found that while each surface produced charges of like character there appeared to be a variation of 250 percent in the magnitude of the piezoelectric charge. No regularity of distribution could be detected on any of the crystals.

The crystal was then subjected to test for the production of piezoelectric charge over the entire surface. The resulting charge is given in Table I, crystal I (a). The crystal was next cut into three pieces of unequal size and the piezoelectric charge of each measured with the resulting charge as given in (b), (c), (d), Table I. The largest of these three pieces was cut into two pieces and the charge determined (e) and (f), Table I. It can be seen that the charge produced varies very markedly among the separate pieces and that the charge for the whole piece is smaller than that for any one. No explanation of this peculiarity is available. To explain this phenomenon satisfactorily it will be necessary to investigate more samples of quartz; further work on this is in progress.

In order to show the accuracy with which the measurements could be repeated, crystal number 2 was measured on different days and under as nearly identical conditions as possible. Both the positive and negative faces were tested with the result that the charge on the positive face appeared to be uniformly smaller than that on the negative as is shown in crystal 2(*a*), (*b*), (*c*), (*d*), (*e*), (*f*), (*g*) of Table I. The results taken for the different days on the negative side of the quartz agree with each other within the limit of error that one would expect in this type of experiment, and the same may be said of the positive side.

As an example of the difference of charge produced on different samples of quartz, 3 and 4 of Table I are crystals cut from optically perfect material in as nearly the same manner as possible. They were subjected to test within a very few minutes of each other thus insuring as nearly identical conditions as possible, and it is seen from the table that they differ in charge by a large amount. This appears to be typical of the behaviour of quartz and is perhaps to be explained by the imperfections in crystal structure mentioned in an earlier paragraph.

TEMPERATURE COEFFICIENT OF THE PIEZOELECTRIC EFFECT OF QUARTZ

In the experiment on the variation of the piezoelectric effect with temperature, the specimen was placed on table *D*, Fig. 2 and the electric furnace placed over it. The apparatus was suitably shielded electrically and the temperature measured by a chromel-nichrome thermocouple. The charge was produced by lifting a 500 gm weight from the quartz. The temperature was varied by convenient intervals to a point well above 573°C, thus passing the transformation point of α-quartz to β-quartz. The apparatus was brought to the desired temperature and allowed to stand until temperature equilibrium conditions and been reached. Six readings were taken and the mean of the six was used as the recorded result. Two crystals from the different pieces of quartz were used.

The curves in Fig. 6 exhibit the results, where the abscissas are the temperatures of the quartz and the ordinates are electrometer deflections. The upper curves were taken with ascending and the lower with descending temperatures. It is seen that the curves for both crytsals are of the same character, starting from approximately the same value at room temperature and rising to a maximum at about 60°C. From the maximum the curves descend slowly until a temperature of about 300°C is attianed. Beyond this point they descend rapidly, reaching low values in one case at a temperature of 440°C and in the other case at 480°C. Beyond these points the piezoelectric effect is extremely small and in the neighborhood of 550°C has practically disappeared.

Upon cooling no deflection of the electrometer could be detected until the apparatus had cooled down to 280°C, and then there appeared a very rapid rise to a maximum value at 60°C and from here to room temperature a decreasing charge was observed. The maximum reached on cooling was approximately one half in one case and two thirds in the other of the maximum reached on heating, and the resulting piezoelectric effect at room temperature after cooling was about one half of the value of that before subjecting the crystal to heating. It was found that after the apparatus had remained untouched for 24 hours that both crystals had returned to their previous piezoelectric condition.

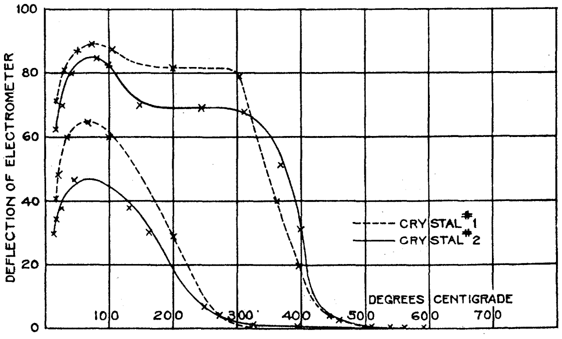

Fig. 6. Curves showing the effect of temperature on the piezoelectric effect in quartz.

It was thought that the peculiarities of the curve might be due to the oxidation of the copper electrode, although this was very slight, but on substituting an aluminum rod for copper the same results were obtained.

The maximum in the curve has no evident explanation and was not expected. The lag in the piezoelectric effect however, is a phenomenon to perhaps be expected, since other effects of similar nature, for example in the moduli of elasticity, have been observed in the transformation of β-quartz to α-quartz.

I wish to express my thanks to Dr. E. O. Hulburt for suggesting the problem and for his keen interest and help in the work.

Heat and Light Division,
Naval Research Laboratory,
September 10, 1926.