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Properties of Monoclinic Crystals

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Two crystals of the monoclinic sphenoidal class have been found which have modes of vibration with zero temperature coefficients of frequency, and this property together with the high electromechanical coupling and the high Q's make it appear probable that these crystals may have considerable use as a substitute for quartz which is difficult to obtain in large sizes. These crystals are ethylene diamine tartrate ($C_6H_{14}N_2O_6$) and dipotassium tartrate ($K_2C_4H_4O_6$, $\frac{1}{2}H_2O$). Complete measurements of the elastic, piezoelectric, and dielectric constants of the dipotassium tartrate (DKT) crystal are given in this paper. The crystal has 4 dielectric constants, 8 piezoelectric constants, and 13 elastic constants. A discussion is given in the appendix of the method of measuring these constants by the use of 18 properly oriented crystals.

I. INTRODUCTION

As part of the program for investigating promising piezoelectric crystals, measurements have been made of a number of piezoelectric crystals occurring in the various crystallographic classes. It has been found that the less symmetric classes give greater possibilities in obtaining low temperature coefficients because with the larger number of elastic constants a greater possibility exists of balancing temperature coefficients between the various constants and obtaining zero temperature coefficient crystals. In particular two crystals of the monoclinic sphenoidal class have been found which have modes of vibration with zero temperature coefficients of frequency, and this property together with the high electromechanical coupling and the high Q's (or low internal dissipation) make it appear likely that these crystals may have considerable use as substitutes for quartz, which is difficult to obtain in large sizes. These two crystals are ethylene diamine tartrate* (which has been given the designation EDT) and dipotassium tartrate (which has been given the designation DKT).

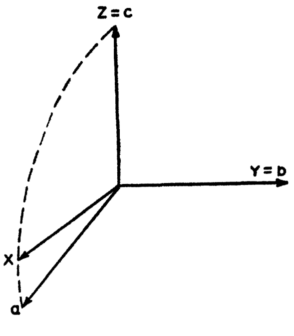

FIG. 1. Method of relating rectangular X, Y, Z axes to a, b, c crystallographic axes of a monoclinic crystal.

It is the purpose of this paper to derive the fundamental constants for a monoclinic crystal and to show how they are measured. This process is illustrated completely for one of these crystals, dipotassium tartrate ($K_2C_4H_4O_6$, $\frac{1}{2}H_2O$). This crystal forms in the monoclinic sphenoidal class which has as its only element of symmetry the b or Y crystallographic axis, which is an axis of binary symmetry. As a consequence there are four dielectric constants, eight piezoelectric constants, and thirteen elastic constants. To obtain all of these constants requires measuring the properties of eighteen carefully oriented crystal cuts. Since this is the first time that all of the properties of a monoclinic crystal have been measured by dynamic methods, a complete description of the process is given in the appendix.

II. MONOCLINIC CRYSTALS AND THEIR RESULTING PIEZOELECTRIC EQUATIONS

Monoclinic crystals are characterized by having two crystallographic axes b and c at right angles to each other, and a third axis a which makes an angle different from 90° with the other two. The c axis lies along the shortest direction of the unit cell while the b axis is the axis of twofold symmetry. In measuring the properties of a crystal, the calculation comes out much more

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* A paper on the properties of this crystal is in course of preparation.

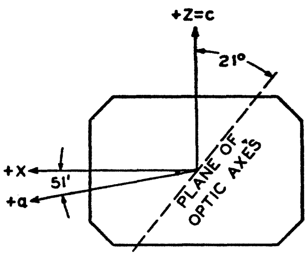

FIG. 2. Relation of $+X$ and $+Z$ axes to plane of optic axes.

simply for a right-angled system of coordinates. As shown by Fig. 1, the method chosen[1] for relating the right-angled X, Y, Z system of axes to the a, b, c crystallographic axes of the crystallographer is to make Z coincide with c, Y with b, and to have the X axis lie in the plane of the b axis and at an angle of 51′ above a for DKT.

The X, Y, Z axes form a right-angled system of axes. Since b is the binary axis, it is necessary to have a convention for specifying which end of the axis is positive. As shown in a companion paper by W. L. Bond[2] this can be done by locating the optic axis of the crystal. A monoclinic crystal is a biaxial crystal and the plane that contains these axes is found to be parallel to the b or Y crystallographic axis. As shown by Fig. 2, the plane of the optic axes lies at a clockwise direction of 21° from the c or Z crystallographic axis. Since X lies at a counterclockwise angle of 90° from c and $(+b=+Y)$ makes a right-angle system of coordinates with the X and Z axes, the measurement determines the positive directional of all three axes. Oriented crystal cuts are usually specified by x-ray orientation procedures as discussed in the above paper.[2]

These crystals were grown from a supersaturated solution by A. N. Holden. Holden finds that the water of crystallization in DKT is quite tightly bound and experimentally it has been found that no noticeable dehydration takes place at 80°C over a week's time. At about 150°C the vapor pressure of DKT reaches atmospheric and will cause bubbling in an oil bath. The usual crystal habit is that shown by Fig. 3. The crystal has two cleavage planes lying along planes determined by the three crystallographic axes. However, these cleavages are not sufficiently bad to cause much trouble in processing these crystals.

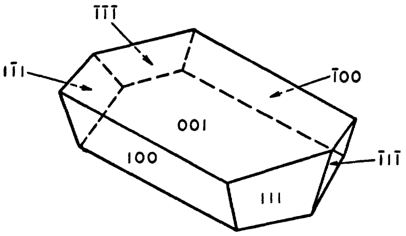

FIG. 3. Crystal habit for DKT crystals.

The Voigt form of writing the piezoelectric equations for a monoclinic sphenoidal crystal is as shown in Eq. (1). In this equation T_1 to T_6 represent the six stresses and S_1 to S_6, the six strains. σ represents the electric displacement $D/4\pi$ in the interior of the crystal and the normal component of σ is the surface charge.

$$\begin{aligned}
S_1&=s_{11}{}^ET_1+s_{12}{}^ET_2+s_{13}{}^ET_3+s_{15}{}^ET_5+d_{21}E_y,\\
S_2&=s_{12}{}^ET_1+s_{22}{}^ET_2+s_{23}{}^ET_3+s_{25}{}^ET_5+d_{22}E_y,\\
S_3&=s_{13}{}^ET_1+s_{23}{}^ET_2+s_{33}{}^ET_3+s_{35}{}^ET_5+d_{23}E_y,\\
S_4&=s_{44}{}^ET_4+s_{46}{}^ET_6+d_{14}E_x+d_{34}E_z,\\
S_5&=s_{15}{}^ET_1+s_{25}{}^ET_2+s_{35}{}^ET_3+s_{55}{}^ET_5+d_{25}E_y,\\
S_6&=s_{46}{}^ET_4+s_{66}{}^ET_6+d_{16}E_x+d_{36}E_z,\\
\sigma_x&=\frac{\epsilon_{11}{}^TE_x}{4\pi}+\frac{\epsilon_{13}{}^TE_z}{4\pi}+d_{14}T_4+d_{16}T_6,\\
\sigma_y&=\frac{\epsilon_{22}{}^TE_y}{4\pi}+d_{21}T_1+d_{22}T_2+d_{23}T_3+d_{25}T_5,\\
\sigma_z&=\frac{\epsilon_{13}{}^TE_x}{4\pi}+\frac{\epsilon_{33}{}^TE_z}{4\pi}+d_{34}T_4+d_{36}T_6,
\end{aligned}\tag{1}$$

where the superscripts E over the elastic compliances indicate that they are to be measured with the applied fields held constant or zero. When there are two applied fields both of these fields have to be held constant or zero to obtain the Voigt elastic compliances. The superscripts T for the dielectric constants indicate that they are to be measured for no stresses applied, i.e., that they are the "free" dielectric constants.

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[1] This system of relating rectangular axes to crystallographic axes has been standardized by a committee on piezoelectric crystals of the Institute of Radio Engineers, under the chairmanship of Professor W. G. Cady. They have also standardized the symbols and nomenclature used in this paper.

[2] Paper in course of preparation.

TABLE I. X cut crystals of DKT.

	Shear mode				Longitudinal modes			
	Length along Z L = 20.20 mm W = 4.25 mm T = 0.91 mm		Length 22.5° from Y L = 20.01 mm W = 3.21 mm T = 0.896 mm		Length 45° from Y L = 19.65 mm W = 3.2 mm T = 0.90 mm		Length 67.5° from Y L = 21.0 mm W = 3.23 mm T = 0.912 mm	
Temperature in degrees C	f_R	Δf	f_R	Δf	f_R	Δf	f_R	Δf
+80	235300	1000	89160	180	85100	280	81000	150
+70	236350		89560		85500		81370	
+60	237500	1000	89980	170	85980	270	81750	150
+50	238600		90380		86340		82120	
+40	239600	1000	90800	170	86760	260	82480	140
+30	240650		91240		87210		82860	
+20	241750	975	91690	160	87670	250	83260	140
+10	242750		92100		88030		83610	
0	243800	975	92440	160	88390	240	83940	130
−10	244700		92770		88690		84280	
−20	245600	960	93100	150	89030	220	84520	130
−30	246500		93400		89350		84850	
−40	247400	930	93690	150	89630	220	85120	120
−50	248250		93960		89940		85420	
−60	249100	930	94270	130	90240	210	85700	110
−70	249950		94570		90610		85980	
−80	250700	930	94860	140	90910	210	86260	110

TABLE II. Z cut crystals of DKT.

	Shear mode				Longitudinal modes			
	Length along Y L = 19.84 mm W = 4.27 mm T = 0.90 mm		Length 22.5° from Y L = 19.61 mm W = 3.21 mm T = 0.863 mm		Length 45° from Y L = 19.96 mm W = 3.13 mm T = 0.910 mm		Length 67.5° from Y L = 19.96 mm W = 3.32 mm T = 0.886 mm	
Temperature in degrees C	f_R	Δf	f_R	Δf	f_R	Δf	f_R	Δf
+80	257500	5600	91030	920	88225	1600	101840	1110
+70	257600		91290		88300		102040	1130
+60	257600	5750	91520	980	88375	1775	102180	1200
+50	257500		91760		88450		102280	
+40	257400	5900	92000	1020	88500	1900	102380	1400
+30	257200		92200		88550		102450	
+20	257000	6400	92420	1100	88600	2000	102540	1600
+10	256700		92620		88630		102620	
0	256450	7000	92810	1200	88660	2125	102680	1720
−10	256150		92990		88660		102720	
−20	255850	7400	93150	1300	88650	2275	102740	1880
−30	255500		93310		88640		102760	
−40	255100	7900	93450	1400	88610	2450	102780	2000
−50	254700		93600		88560		102800	
−60	254250	8400	93720	1500	88490	2650	102800	2150
−70	253800		93840		88425		102770	
−80	253300	8900	93960	1600	88350	2875	102740	2200

TABLE III. *Y* cut crystals of DKT.

	Shear mode		Longitudinal modes					
	Length along Z $L=14.52$ mm $W=2.95$ mm $T=1.05$ mm		Length 22.5° from X $L=19.95$ mm $W=3.71$ mm $T=1.03$ mm		Length 45° from X $L=20.32$ mm $W=4.03$ mm $T=1.05$ mm		Length 67.5° from X $L=12.75$ mm $W=2.51$ mm $T=1.02$ mm	
Temperature in degrees C	f_R	Δf	f_R	Δf	f_R	Δf	f_R	Δf
+80	401500	1000	123760	780	101460	1030	135950	950
+70	402850		124000		101660		136550	
+60	404000	1000	124210	750	101880	1010	137150	940
+50	405000		124440		102080		137700	
+40	406100	1000	124650	730	102300	990	138200	930
+30	407100		124860		102500		138710	
+20	408200	1000	125100	710	102700	980	139240	920
+10	409200		125300		102900		139770	
0	410100	950	125510	700	103120	970	140350	910
−10	411100		125730		103320		140820	
−20	412050	950	125950	680	103530	960	141220	900
−30	413000		126160		103720		141610	
−40	413950	950	126370	670	103940	960	142000	880
−50	414950		126600		104140		142400	
−60	415900	950	126810	640	104340	930	142800	870
−70	416900		127040		104650		143220	
−80	417850	950	127250	620	104750	910	143650	850

TABLE IV. Oblique cuts of DKT.

	Width parallel to Z—length and thickness 45° from X and Y. Shear mode $L=20.28$ mm $W=3.18$ mm $T=0.895$ mm		Width parallel to X—length 45° from Y and Z. Longitudinal mode $L=11.13$ mm $W=3.20$ mm $T=0.90$ mm		Orientation. See Fig. 9 $L=20.09$ mm $W=3.195$ mm $T=0.90$ mm		Length along Y width 45° from X and Y. Face shear mode $L=20.29$ mm $W=3.2$ mm $T=0.89$ mm	
Temperature in degrees C	f_R	Δf	f_R	Δf	f_R	Δf	f_R	Δf
+80	328100	900	149900	365	86220	280	335000	7350
+70	329500		150810		86440		336100	
+60	330700	900	151600	365	86650	310	336600	6800
+50	331800		152400		86870		337900	
+40	332950	930	153100	370	87100	350	338500	7100
+30	334000		153800		87350		339500	
+20	334950	930	154500	380	87575	350	340500	7350
+10	335900		155200		87800		341200	
0	336850	950	155800	385	88000	385	341900	8000
−10	337800		156400		88200		342600	
−20	338250	1000	156950	415	88390	385	343300	8470
−30	339700		157510		88575		344000	
−40	340600	1050	158050	430	88750	420	344600	9000
−50	341550		158550		88925		345000	
−60	342500	1060	159050	435	89050	490	345520	9640
−70	343400		159500		89175		346000	
−80	344400	1120	159900	450	89300	525	346400	10200

For ferroelectric type crystals it has been found that equations which relate the piezoelectric effect to the electrical displacement or the surface charge (the normal component displacement $D/4\pi$ equals the surface charge at the crystal surface) are more fundamental than those based on the field. By eliminating the fields from the first six equations of (1), by substituting in the displacements from the last three equations we have

$$\begin{aligned}
S_1&=s_{11}{}^DT_1+s_{12}{}^DT_2+s_{13}{}^DT_3+s_{15}{}^DT_5+g_{21}\sigma_y,\\
S_2&=s_{12}{}^DT_1+s_{22}{}^DT_2+s_{23}{}^DT_3+s_{25}{}^DT_5+g_{22}\sigma_y,\\
S_3&=s_{13}{}^DT_1+s_{23}{}^DT_2+s_{33}{}^DT_3+s_{35}{}^DT_5+g_{23}\sigma_y,\\
S_4&=s_{44}{}^DT_4+s_{46}{}^DT_6+g_{14}\sigma_x+g_{34}\sigma_z,\\
S_5&=s_{15}{}^DT_1+s_{25}{}^DT_2+s_{35}{}^DT_3+s_{55}{}^DT_5+g_{25}\sigma_y, \qquad (2)\\
S_6&=s_{46}{}^DT_4+s_{66}{}^DT_6+g_{16}\sigma_x+g_{36}\sigma_z,\\
E_x&=4\pi\beta_{11}{}^T\sigma_x+4\pi\beta_{13}{}^T\sigma_z-g_{14}T_4-g_{16}T_6,\\
E_y&=4\pi\beta_{22}{}^T\sigma_y-g_{21}T_1-g_{22}T_2-g_{23}T_3-g_{25}T_5,\\
E_z&=4\pi\beta_{13}{}^T\sigma_x+4\pi\beta_{33}{}^T\sigma_z-g_{34}T_4-g_{36}T_6,
\end{aligned}$$

TABLE V. Free dielectric constants of DKT.

Temperature in degrees C	Dielectric constant normal to X	Dielectric constant normal to Y	Dielectric constant normal to Z	Dielectric constant normal to a plane making 45° angle with X and Z
+80	6.64	5.97	6.53	6.57
+70	6.61	5.94	6.52	6.55
+60	6.57	5.91	6.51	6.53
+50	6.54	5.89	6.51	6.52
+40	6.51	5.86	6.50	6.50
+30	6.48	5.83	6.49	6.48
+20	6.44	5.80	6.49	6.47
+10	6.41	5.78	6.48	6.45
0	6.38	5.75	6.47	6.43
−10	6.35	5.72	6.47	6.41
−20	6.31	5.69	6.46	6.39
−30	6.28	5.66	6.45	6.38
−40	6.25	5.64	6.45	6.36
−50	6.22	5.61	6.46	6.34
−60	6.19	5.58	6.47	6.34
−70	6.15	5.55	6.48	6.33
−80	6.12	5.52	6.50	6.32
−90	6.09	5.49	6.52	6.31
−100	6.05	5.47	6.54	6.31

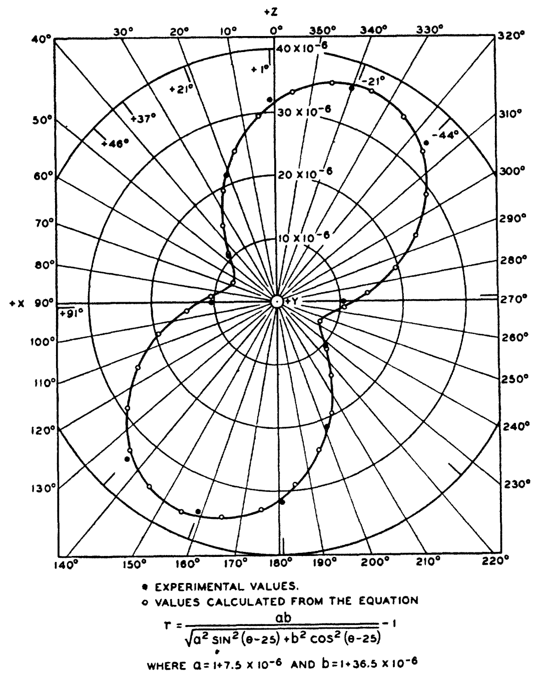

FIG. 4. Average temperature expansion coefficient for DKT crystals in the XZ plane.

where the $\beta_{ij}{}^T$ constants are the "free" dielectric impermeabilities, which are related to the dielectric constants $\epsilon_{ij}{}^T$ by the equations

$$\beta_{11}{}^T=\frac{\epsilon_{33}{}^T}{\epsilon_{11}{}^T\epsilon_{33}{}^T-(\epsilon_{13}{}^T)^2};\quad \beta_{13}{}^T=\frac{-\epsilon_{13}{}^T}{\epsilon_{11}{}^T\epsilon_{33}{}^T-(\epsilon_{13}{}^T)^2};$$
$$\beta_{22}{}^T=\frac{1}{\epsilon_{22}{}^T};\quad \beta_{33}{}^T=\frac{\epsilon_{11}{}^T}{\epsilon_{11}{}^T\epsilon_{33}{}^T-(\epsilon_{13}{}^T)^2}. \qquad (3)$$

The relations between the displacement and field elastic compliances and between the d and g piezoelectric constants are discussed in detail in the appendix.

III. MEASUREMENT OF THE PROPERTIES OF DKT

The preferred orientations for measuring crystal properties and the elastic, piezoelectric, and dielectric constants associated with each cut have been discussed in detail in the appendix, Section VI. It is the purpose of this section to record the measured results for the cuts and to give the final constants as calculated from the measurements. The resonant and anti-resonant frequencies, the resistance at resonance and the capacitance at low frequencies have been meas-

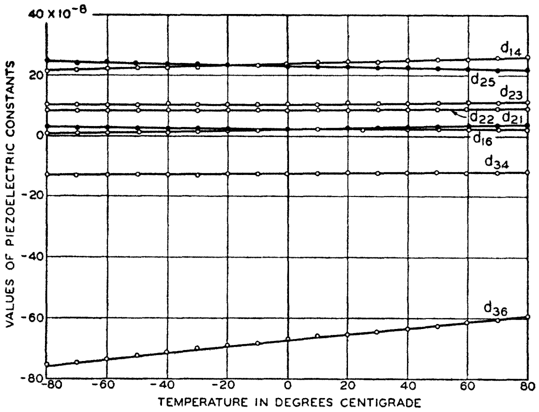

FIG. 5. Piezoelectric constants of DKT crystals as a function of temperature.

ured for all crystal cuts over a temperature range from −80°C to +80°C.

The first series of cuts is a set of four crystals cut normal to X with their lengths along the Z axis and at 22.5°, 45°, and 67.5° from Z. Table I shows the measured resonance frequencies, and the separation of the resonant and anti-resonant frequencies all made in a holder which is shielded so that no stray capacity has to be allowed for. Table II shows similar data for Z cut crystals and Table III for Y cut crystals. In order to complete the measurements several double orientation crystals have to be used and the orientations and data are given by Table IV. Finally Table V shows a measurement of the dielectric constants of four crystals. These are measured at 1000 cycles and represent the "free" dielectric constants. From these data and the data of the temperature[3] expansion coefficients shown by Fig. 4 all of the properties of the crystal can be determined.

In order to illustrate the method, calculations are made at room temperature of all of the constants. From Table I we find that the resonant frequency and the separation of resonant and anti-resonant frequency for a crystal cut normal to the X axis, with its length 45° from the Y and Z axes and with the dimension $L=19.65$ mm; $W=3.2$ mm; $T=0.90$ mm, are at 20°C, $f_R=87670$, $(f_A-f_R)=250$ cycles. From Table V the free dielectric constant for this crystal is 6.44. From Eq. (50) of the appendix the coefficient of coupling k is equal to

$$k=\frac{\pi}{2}\left(\frac{\Delta f}{f_R}\right)^{\frac{1}{2}}=\frac{\pi}{2}\left(\frac{250}{87670}\right)^{\frac{1}{2}}=0.084. \tag{4}$$

The frequency constant for the plated crystal is $f_R l=172.1$ kc cm$=f_M{}^E$. Since the density is 1.988, this gives a value for the elastic compliance at constant field along the X axis equal to

$$s_{22_{45^\circ}}{}^{E'}=\frac{1}{(2f_M{}^E)^2\rho}=4.24\times10^{-12}\ \text{cm}^2/\text{dyne}. \tag{5}$$

From this value and the free dielectric constant (6.44) we have from Eq. (17) of the appendix

$$d_{12}'=\left(\frac{\epsilon_{11}{}^T}{4\pi}s_{22}{}^E\right)^{\frac{1}{2}}k=\pm12.35\times10^{-8}\ \text{c.g.s. unit}. \tag{6}$$

But from Eq. (91) of the appendix $d_{12}'=d_{14}/2$ so that the fundamental constant $d_{14}=\pm24.7\times10^{-8}$. As will be shown later this sign is positive, and the value of d_{14} calculated over a temperature range is shown plotted by Fig. 5. Performing the same operations on the crystals cut at 22.5° from Y and 67.5° from Y, we find

$$s_{22_{22.5}}{}^E=3.73\times10^{-12};\quad s_{22_{67.5}}{}^E=4.09\times10^{-12}. \tag{7}$$

Since from Eq. (84) in the appendix, the elastic constant $s_{22}{}^{E'}$ satisfies the equation

$$s_{22}{}^{E'}=s_{22}{}^E\cos^4\theta+(2s_{23}{}^E+s_{44}{}^E)\sin^2\theta\cos^2\theta+s_{33}{}^E\sin^4\theta, \tag{8}$$

these three values are enough to determine the fundamental constants $s_{22}{}^E$, $s_{33}{}^E$, $(2s_{23}{}^E+s_{44}{}^E)$. The formulae are

$$\begin{aligned} s_{22}{}^E&=1.707s_{22_{22.5}}{}^E-s_{22_{45}}{}^E+0.293s_{22_{67.5}}{}^E;\\ s_{33}{}^E&=0.293s_{22_{22.5}}{}^E-s_{22_{45}}{}^E+1.707s_{22_{67.5}}{}^E;\\ (2s_{23}{}^E+s_{44}{}^E)&=6s_{22_{45}}{}^E-2(s_{22_{22.5}}{}^E+s_{22_{67.5}}{}^E). \end{aligned} \tag{9}$$

From these formulae and the values of Eq. (7) we obtain

$$\begin{aligned} &s_{22}{}^E=3.395\times10^{-12};\quad s_{33}{}^E=3.907\times10^{-12};\\ &(2s_{23}{}^E+s_{44}{}^E)=9.684\times10^{-12}. \end{aligned} \tag{10}$$

The first crystal of Table I is a face shear vibrating crystal whose frequency is determined

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[3] The temperature expansion coefficients of DKT crystals have been measured by Miss E. J. Armstrong.

by the width of the crystal. From Eqs. (105) and (106) of the appendix, the frequency is determined by

$$f=\frac{1}{2l_w}\left(\frac{c_{44}{}^{c,E}}{\rho}\right)^{\frac{1}{2}} \tag{11}$$

and the fundamental elastic constant $s_{44}{}^E$ by the equation

$$s_{44}{}^E=1/c_{44}{}^{c,E}. \tag{12}$$

From the measured values of Table I,

$$c_{44}{}^{c,E}=8.35\times10^{10}\text{ dynes/cm}^2;\quad k=0.100;\quad \epsilon_{11}{}^T=6.44. \tag{13}$$

Hence

$$s_{44}{}^E=11.9\times10^{-12}\text{ cm}^2\text{/dyne};\quad d_{14}=24.7\times10^{-8}. \tag{14}$$

This checks the value of d_{14} obtained from the 45° X cut crystal. It also shows that the shear mode driven by a shear elastic constant has a higher coupling than a 45° longitudinal cut driven by the same shear constant.

When these constants are measured over a wide temperature range, it is necessary to take account of the coefficients of temperature expansion. This changes not only the length of the frequency determining direction, but also changes the density ρ since the total volume of the crystal changes with temperature. The average of the temperature coefficients measured from $-40°$ to $+80°$C are shown by Fig. 4. In the XZ plane, the coefficient follows the dumbbell shape with its major axis at an angle of about -26 degrees from the Z axis. This shape represents the difference between a circle at 25°C and the ellipse that the circle expands into at different temperatures. The temperature coefficient along the Y axis is 44.8 parts per million per degree centigrade. When it is desired to obtain the temperature expansion coefficient for any other angle, say in a plane containing the Y axis and making an angle θ with the Z axis, with the direction making an angle φ with the Y axis, the coefficient is obtained by reading the coefficient T_θ for the angle θ in the XY plane and substituting in the formula

$$T_l=T_\theta\sin^2\varphi+T_y\cos^2\varphi, \tag{15}$$

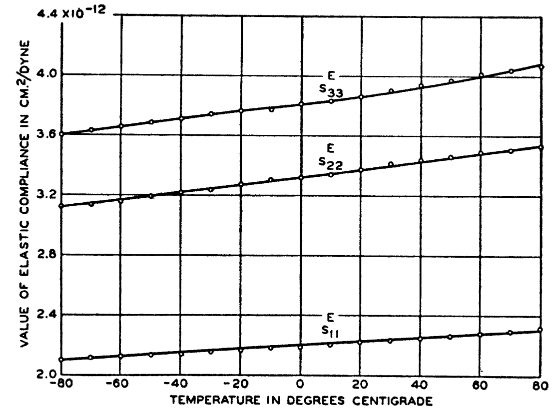

FIG. 6. Three extensional moduli of compliance measured as a function of temperature.

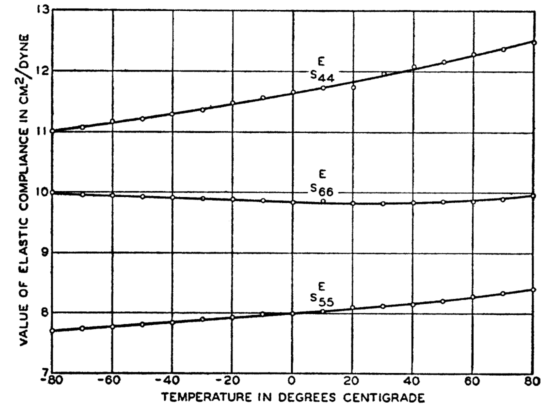

FIG. 7. Three shearing moduli of compliance for DKT measured as a function of temperature.

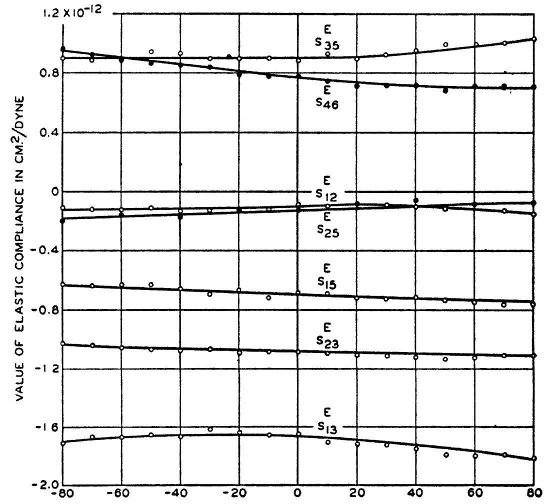

FIG. 8. Seven cross coupling moduli of compliances measured as a function of temperature.

where T_y is the temperature coefficient along the Y axis. The total increase in volume is

$$V = V_0[1+T_x\Delta\Theta][1+T_y\Delta\Theta][1+T_z\Delta\Theta] \doteq 1+(T_x+T_y+T_z)\Delta\theta, \quad (16)$$

where $\Delta\theta$ is the increment in temperature measured from 25°C. The sum of the three temperature coefficients is 87.8×10^{-6}. Hence since the total mass of the crystal remains constant the temperature coefficient of density is

$$T_\rho = -87.8\times 10^{-6} \text{ per °C}. \quad (17)$$

From the frequency equation for a longitudinal mode

$$f = \frac{1}{2l}\left(\frac{1}{\rho s}\right)^{\frac{1}{2}} \quad (18)$$

the correction to the elastic compliance s is

$$s = \frac{1}{\rho(2lf)^2} = \frac{1}{\rho_0[1-87.8\times 10^{-6}\Delta\Theta][2fl_0(1+T_l\Delta\Theta)]^2} = \frac{1+(87.8-2T_l)\times 10^{-6}\Delta\Theta}{\rho_0(2fl_0)^2}, \quad (19)$$

where $\Delta\Theta$ is the change in temperature from 25°C, ρ_0 the density measured at 25°C, and l_0 the length measured at 25°C. With this correction for temperature coefficient, the elastic constants $s_{22}{}^E$, $s_{33}{}^E$, $s_{44}{}^E$, and $s_{23}{}^E$ are shown plotted on Figs. 6–8.

From the data of Table II for Z cut crystals a similar process determines the constants $s_{11}{}^E$, $s_{22}{}^E$, $(2s_{12}{}^E+s_{66}{}^E)$ and $s_{66}{}^E$. At room temperature these become

$$s_{11}{}^E = 2.218\times 10^{-12}; \quad s_{22}{}^E = 3.404\times 10^{-12};$$
$$2s_{12}{}^E+s_{66}{}^E = 9.64; \quad s_{66}{}^E = 9.81; \quad (20)$$
$$s_{12}{}^E = -0.085.$$

This provides a check for $s_{22}{}^E$ measured for Z cuts and checks within less than one percent. Over a temperature range the values of $s_{11}{}^E$, $s_{22}{}^E$, $s_{12}{}^E$, and $s_{66}{}^E$ are shown plotted on Figs. 6–8. The value of d_{36} obtained for the Z cut is the largest piezoelectric constant for the crystal and reaches a value of 66.4×10^{-8} c.g.s. unit. As shown by the measurement of oblique cuts, its sign is negative compared to d_{14}. d_{36} increases very considerably as the temperature decreases and may indicate the presence of hydrogen bonds. The large value of d_{36} coupled with the low temperature coefficients for crystals cut normal to the Z axis (particularly the 45° Z cut) make such crystals very useful in filters and in the control of low frequency oscillators.

For crystals cut normal to the Y axis of a monoclinic crystal, the longitudinal elastic constant varies with angle according to the equation

$$s_{33}{}'^E = s_{33}{}^E \cos^4\psi + 2s_{35}{}^E \cos^3\psi \sin\psi + (2s_{13}{}^E+s_{55}{}^E)\sin^2\psi\cos^2\psi + 2s_{15}{}^E \sin^3\psi\cos\psi + s_{11}{}^E\sin^4\psi. \quad (21)$$

The derivation of this equation is given in the appendix, Eq. (86). The values of $s_{33}{}^E$ and $s_{11}{}^E$ are given in Fig. 6 so that the data for the three longitudinal crystals are sufficient to determine $s_{35}{}^E$, $(2s_{13}{}^E+s_{55}{}^E)$ and $s_{15}{}^E$ which are shown plotted on Figs. 7 and 8. The equation for the piezoelectric constants of longitudinal crystals cut normal to the Y axis is

$$d_{12}' = d_{21}\sin^2\psi + d_{23}\cos^2\psi + \frac{d_{25}}{2}\sin 2\psi. \quad (22)$$

From the values of coupling and the dielectric constants for the three crystals, we find

$$d_{21} = +2.2\times 10^{-8}; \quad d_{23} = +10.4\times 10^{-8}; \quad d_{25} = +22.4\times 10^{-8}. \quad (23)$$

All constants have the same sign. The sign of d_{23} was determined by squeeze tests on the crystal to be a positive charge delivered along the positive Y axis for an extension along the Z axis.

The two remaining elastic cross constants $s_{25}{}^E$ and $s_{46}{}^E$ have to be evaluated by employing oblique cuts that do not lie along or normal to any of the three crystallographic axes. $s_{46}{}^E$ can be determined by using the face shear mode of a crystal cut with its length along Y and its width

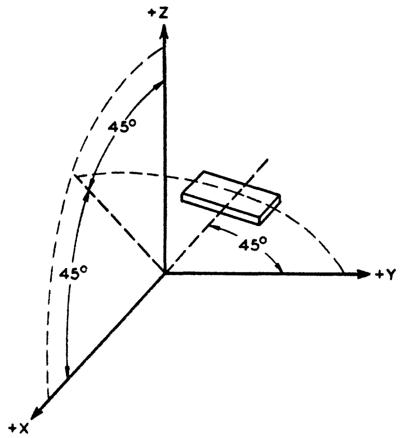

FIG. 9. Doubly oriented DKT crystal.

at 45° between the positive X and Z axes, for as shown by Eqs. (105)–(107) of the appendix, the frequency of the unplated crystal determines the elastic constant

$$s_{66}^{E\prime}=\frac{s_{66}^{E}-2s_{46}^{E}+s_{44}^{E}}{2}. \tag{24}$$

From the data of the last crystal of Table IV, we find $s_{46}^{E}=0.74\times10^{-12}$ at 20°C. The electromechanical coupling factor as calculated from the resonant and anti-resonant frequencies is

$$k=0.225. \tag{25}$$

Since from Eq. (108) the piezoelectric constant driving this mode is

$$\mathrm{d}_{14}'=\frac{(d_{14}+d_{16}-d_{34}-d_{36})}{2} \tag{26}$$

and the dielectric constant from Table V is 6.47, we find

$$d_{14}'=52.6\times10^{-8}. \tag{27}$$

Since d_{14} and d_{36} have been found equal to 24.7×10^{-8} and -66.4×10^{-8}, we find

$$d_{16}-d_{34}=14\times10^{-8}. \tag{28}$$

The constant s_{25}^{E} was determined by measuring the resonant frequency of a crystal oriented as shown by Fig. 9. It is shown in the appendix, Eq. (87), that the frequency of a plated crystal is given by

$$f=\frac{1}{2l}\left(\frac{1}{\rho s_{22}^{E}}\right)^{\frac{1}{2}}, \tag{29}$$

where

$$s_{22}^{E\prime}=\tfrac{1}{16}[s_{11}^{E}+s_{33}^{E}+(s_{55}^{E}+2s_{13}^{E})]$$
$$+\tfrac{1}{8}[s_{15}^{E}+s_{35}^{E}+s_{46}^{E}+(s_{44}^{E}+2s_{23}^{E})$$
$$+(s_{66}^{E}+2s_{12}^{E})]+\tfrac{1}{4}[s_{22}^{E}+s_{25}^{E}].$$

Since all the values are known except s_{25}^{E}, the data for the third crystal of Table IV yield the value

$$s_{25}^{E}=-0.12\times10^{-8}. \tag{30}$$

The second crystal of Table IV provides a check on the elastic constant for a direction in the YZ plane halfway between the two axes. The value found is 4.19×10^{-12} dyne/cm^2 which checks the value for a 45° X cut crystal shown by Table I. The piezoelectric constant driving this mode is from Eq. (97) of the appendix

$$d_{12}'=0.3535[d_{23}+d_{22}-d_{34}]. \tag{31}$$

From the data of Table IV, $d_{12}'=11.1\times10^{-8}$ and since d_{23} is known, we have

$$d_{22}-d_{34}=21.0\times10^{-8}. \tag{32}$$

This value together with the data of Eq. (28) gives

$$d_{22}-d_{16}=7.0\times10^{-8}. \tag{33}$$

The first crystal of Table IV should have a longitudinal mode driven by the piezoelectric constant (from Eq. (99) of appendix)

$$d_{12}'=-0.3535[d_{21}+d_{22}-d_{16}]. \tag{34}$$

From the values given above this should result in a value of 3.2×10^{-8} which should give a very low coupling. This was verified for no resonance was found for this mode. Driven in a face shear mode this crystal should have a piezoelectric shear constant equal to

$$d_{14}'=\frac{(d_{14}+d_{25})}{2}=23.5\times10^{-8}. \tag{35}$$

From the data of Table IV, the measured value is about 20×10^{-8} which verifies the sign of d_{14} with respect to d_{25}.

Finally the driving constant of the double oriented crystal, Number 3 of Table IV should be according to Eq. (102) of the appendix

$$d_{12}'=0.1768[d_{21}+d_{23}+d_{25}+2d_{22}-(d_{14}+d_{16}+d_{34}+d_{36})]. \quad (36)$$

From the values and signs assigned, we find $d_{12}'=18.5\times10^{-8}$. The measured value from Table IV is 15×10^{-8}, which verifies the sign of d_{36}.

All of the elastic constants are determined except s_{55}^E and all the piezoelectric constants except d_{22} (or d_{16} or d_{34}). To determine s_{55}^E we make use of the data of Table III on the face shear mode of a *Y* cut crystal. As shown in the appendix the elastic constant controlling this mode is a "coupled" constant and the frequency is given by

$$f=\frac{1}{2l_w}\left(\frac{c_{11}{}^{c,E}+c_{55}{}^{c,E}-[(c_{11}{}^{c,E}-c_{55}{}^{c,E})^2+4c_{15}{}^{c,E^2}]^{\frac{1}{2}}}{2\rho}\right)^{\frac{1}{2}}. \quad (37)$$

The method of calculating s_{55}^E from the measured value of the shear mode and the other elastic constants is explained in the appendix. The resultant obtained from the data is

$$s_{55}^E=8.15\times10^{-12}. \quad (38)$$

The values over a temperature range are shown by Fig. 7. With this value s_{13} can be determined and all the elastic constants are given by Figs. 6–8.

To determine the remaining piezoelectric constants, requires measuring the properties of a thickness mode. Either of the two shears S_6 or S_4 can be used or the thickness longitudinal mode. Of these the mode with the largest coupling is the S_4 mode, which is obtained by measuring a *Z* cut crystal, dimensioned so that it has a single mode. This crystal had a coupling of 4.9 percent giving a value of $d_{34}=-12.1\times10^{-8}$. Hence the remaining values are

$$d_{22}=8.9\times10^{-8};\quad d_{16}=1.9\times10^{-8}.$$

Both of these constants are too small to drive modes appreciably, and none were observed. The complete values of the piezoelectric constants over a range of temperature are plotted on Fig. 5.

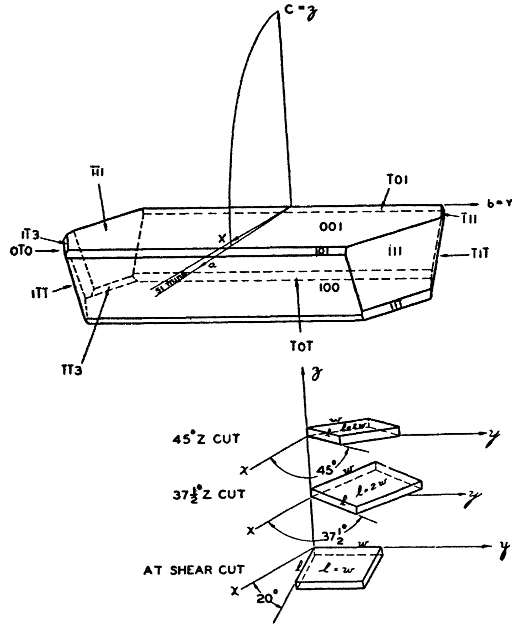

FIG. 10. Orientations of three zero temperature coefficient crystals with respect to the mother crystal. 45° *Z* cut and 37.5° *Z* cut are longitudinal modes. *AT* shear cut is a face shear mode.

IV. DISCUSSION OF PROPERTIES OF DKT CRYSTALS

This crystal has properties that make it a possible substitute for quartz for a number of applications. Three cuts have been found for which large electromechanical couplings are associated with zero temperature coefficients of frequency. These cuts are all perpendicular or nearly perpendicular to the *Z* axis and two of the modes are longitudinal and one a face shear mode. While the coefficient can be made zero at a specified temperature, the deviation from the frequency at the zero temperature coefficient is parabolic as in most zero coefficient quartz crystals. The curvature is several times larger than for quartz crystals. Figure 10 shows these three cuts in relation to the natural crystal.

This crystal shows some evidence of hydrogen bond type of coupling at low temperatures. Figure 11 shows a plot of the inverse of d_{36} for dipotassium tartrate, and indicates only a uniform increase in d_{36} as the temperature is lowered.

Such a curve might be accounted for by a hydrogen bond type of dipole at low temperatures such as occurs for potassium dihydrogen phosphate,[4] and a frozen dipole liberated at a high temperature such as occurs in sodium chlorate and sodium bromate.[5] However, the range in temperature is too small to make this interpretation certain. All the other piezoelectric constants vary less than does d_{36}. The contributions of the different types of dipoles to the dielectric constant is too uncertain to test out the relation found for ammonium dihydrogen phosphate, potassium dihydrogen phosphate, sodium chlorate and sodium bromate, that the piezoelectric stress was proportional to the dipole polarization.

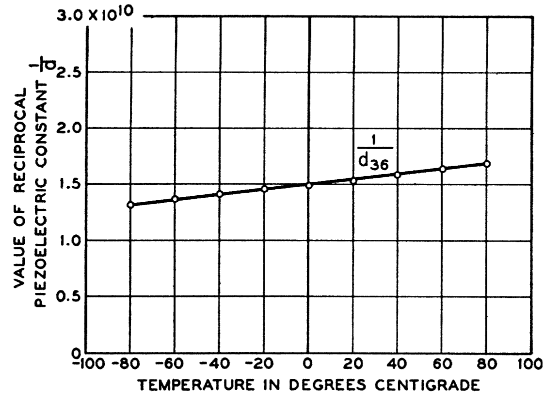

FIG. 11. Inverse of d_{36} plotted over a temperature range.

APPENDIX. CALCULATION OF THE RESONANT FREQUENCIES OF A MONOCLINIC CRYSTAL

I. Introduction

For monoclinic or triclinic crystals, the applied fields and the resulting charge displacements are usually not in the same direction and hence a somewhat extended discussion has to be given for them. It turns out that the piezoelectric constants that are directly measured are the d_{ijm} piezoelectric constants which relate strains to the applied fields. This follows from the fact that the electrical boundary conditions are that the tangential components of the fields of a plated crystal are zero.

It is the purpose of this appendix to investigate the frequencies of longitudinal modes and limiting cases of face shear modes for the purpose of relating the measured frequencies and capacities to the elastic, piezoelectric, and dielectric constants of the crystal. In order to facilitate the calculation the piezoelectric equations are expressed in tensor form, since by doing so, long summation terms are avoided. A short discussion is given of the tensor method of writing the piezoelectric equations.

II. Piezoelectric Equations in Tensor Form

The stress components acting on a unit cube of a solid body are symmetrical and can be written in the form

$$\begin{vmatrix} T_1 & T_6 & T_5 \\ T_6 & T_2 & T_4 \\ T_5 & T_4 & T_3 \end{vmatrix}. \tag{1}$$

These are the three longitudinal stresses and the three shearing stresses. These components form a tensor of the second rank as will be shown. To conform to the usual tensor notation we shall write these components as

$$T_{kl}=\begin{vmatrix} T_{11} & T_{12} & T_{13} \\ T_{12} & T_{22} & T_{23} \\ T_{13} & T_{23} & T_{33} \end{vmatrix} = \begin{vmatrix} T_1 & T_6 & T_5 \\ T_6 & T_2 & T_4 \\ T_5 & T_4 & T_3 \end{vmatrix}. \tag{2}$$

These nine terms form a symmetrical tensor of the second rank for, if we transform them to a rotated system of axes, this transformation takes place according to the tensor transformation formula

$$T_{ij}'=\frac{\partial x_i'}{\partial x_k}\frac{\partial x_j'}{\partial x_l}T_{kl}. \tag{3}$$

In this equation

$$x_i'=x_1',\ x_2',\ x_3'$$

are the coordinates of the rotated set of axes and

$$x_k=x_1,\ x_2,\ x_3$$

are the coordinates of the original axes. The

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[4] W. P. Mason, Phys. Rev. 69, 173–194 (1946).

[5] W. P. Mason, "Elastic, piezoelectric, and dielectric properties of sodium chlorate and sodium bromate," Phys. Rev. 70, 529 (1946).

partial derivates

$$\frac{\partial x_1'}{\partial x_k} = \begin{vmatrix} \frac{\partial x_1'}{\partial x_1} & \frac{\partial x_1'}{\partial x_2} & \frac{\partial x_1'}{\partial x_3} \\ \frac{\partial x_2'}{\partial x_1} & \frac{\partial x_2'}{\partial x_2} & \frac{\partial x_2'}{\partial x_3} \\ \frac{\partial x_3'}{\partial x_1} & \frac{\partial x_3'}{\partial x_2} & \frac{\partial x_3'}{\partial x_3} \end{vmatrix} = \begin{array}{c|ccc|} & x_1 & x_2 & x_3 \\ \hline x_1' & l_1 & m_1 & n_1 \\ x_2' & l_2 & m_2 & n_2 \\ x_3' & l_3 & m_3 & n_3 \end{array} \qquad (4)$$

are the direction cosines between the rotated and the non-rotated systems of axes. In Eq. (3) another tensor convention is used, namely that when an index is repeated on one side of an equation, a summation with respect to the indices 1, 2, 3 is indicated. Both k and l are repeated in Eq. (3). For example in expanded form, letting i' and j' each equal 1, Eq. (3) will expand into

$$\begin{aligned} T_{11}' = \left(\frac{\partial x_1'}{\partial x_1}\right)^2 T_{11} &+ 2\left(\frac{\partial x_1'}{\partial x_1}\frac{\partial x_1'}{\partial x_2}\right) T_{12} \\ &+ 2\left(\frac{\partial x_1'}{\partial x_1}\frac{\partial x_1'}{\partial x_3}\right) T_{13} + \left(\frac{\partial x_1'}{\partial x_2}\right)^2 T_{22} \\ &+ 2\frac{\partial x_1'}{\partial x_2}\frac{\partial x_1'}{\partial x_3} T_{23} + \left(\frac{\partial x_1'}{\partial x_3}\right)^2 T_{33}. \end{aligned} \qquad (5)$$

In ordinary elastic terminology this would be expressed as

$$\begin{aligned} T_1' = l_1^2 T_1 + 2l_1 m_1 T_6 + 2l_1 n_1 T_5 + m_1^2 T_2 \\ + 2m_1 n_1 T_4 + n_1^2 T_3 \end{aligned} \qquad (6)$$

which is the expression given by Love for the transformations of stress from one system of axes to another system. Hence since the stress system is a collection of nine quantities which transfer from one system of axes to another system by the tensor transformation equation, the stress system is a tensor of the second order.

The strain components are usually defined as

$$\begin{gathered} S_1 = \frac{\partial \xi}{\partial x_1}; \quad S_2 = \frac{\partial \eta}{\partial x_2}; \quad S_3 = \frac{\partial \zeta}{\partial x_3}; \\ S_6 = \left(\frac{\partial \eta}{\partial x_1} + \frac{\partial \xi}{\partial x_2}\right); \quad S_5 = \left(\frac{\partial \xi}{\partial x_3} + \frac{\partial \zeta}{\partial x_1}\right); \\ S_4 = \left(\frac{\partial \zeta}{\partial x_2} + \frac{\partial \eta}{\partial x_3}\right), \end{gathered} \qquad (7)$$

where ξ, η, ζ are, respectively, the displacements of the body along the x_1, x_2, x_3 axes, respectively. This set of 9 quantities, however, is not a tensor for it does not satisfy the tensor transformation equation. If, however, we define new strain components as

$$\begin{gathered} S_{11} = S_1 = \frac{\partial \xi}{\partial x_1}; \quad S_{22} = S_2 = \frac{\partial \eta}{\partial x_2}; \quad S_{33} = S_3 = \frac{\partial \zeta}{\partial x_3}; \\ S_{12} = S_{21} = \frac{S_6}{2} = \frac{1}{2}\left(\frac{\partial \eta}{\partial x_1} + \frac{\partial \xi}{\partial x_2}\right); \\ S_{13} = S_{31} = \frac{S_5}{2} = \frac{1}{2}\left(\frac{\partial \xi}{\partial x_3} + \frac{\partial \zeta}{\partial x_1}\right); \\ S_{23} = S_{32} = \frac{S_4}{2} = \frac{1}{2}\left(\frac{\partial \zeta}{\partial x_2} + \frac{\partial \eta}{\partial x_3}\right), \end{gathered} \qquad (8)$$

the symmetrical nine components

$$\begin{vmatrix} S_{11} & S_{12} & S_{13} \\ S_{12} & S_{22} & S_{23} \\ S_{13} & S_{23} & S_{33} \end{vmatrix} \qquad (9)$$

will form a tensor of the second rank.

The generalized Hooke law between the stresses and the strains can be written

$$S_{ij} = s_{ij,kl} T_{kl}, \qquad (10)$$

since $s_{ij,kl}$ or s_{ijkl} is a tensor of the fourth rank. The right-hand side of the equation being the product of a fourth rank tensor by a second rank tensor is a sixth rank tensor, but since it is contracted twice by having k and l in both terms, the resultant of the right-hand side is a second rank tensor. A tensor of the fourth rank will ordinarily have 81 terms, but since S_{ij} and T_{kl} are both symmetrical, only 21 independent terms exist in s_{ijkl}. If we examine this expression and compare term by term with the usual way of writing Hooke's law, given by Eq. (11)

$$\begin{aligned} S_1 = S_{11} = s_{11}T_1 + s_{12}T_2 + s_{13}T_3 \\ + s_{14}T_4 + s_{15}T_5 + s_{16}T_6, \\ \cdots\cdots\cdots\cdots \\ S_6 = 2S_{12} = s_{16}T_1 + s_{26}T_2 + s_{36}T_3 \\ + s_{46}T_4 + s_{56}T_5 + s_{66}T_6 \end{aligned} \qquad (11)$$

and noting that $S_6 = 2S_{12}$, etc., the usual two index compliances correspond to the four index symbol s_{ijkl} provided we replace

$$\begin{matrix} 1 \text{ by } 11, & 2 \text{ by } 22, & 3 \text{ by } 33, \\ 4 \text{ by } 23, & 5 \text{ by } 13, & 6 \text{ by } 12. \end{matrix} \quad (12)$$

However, for any number 4, 5, or 6 the elastic constant s_{ij} has to be divided by two to equal the corresponding s_{ijkl} constant, and if 4, 5, or 6 occurs twice, the diviser has to be 4.

The adiabatic form of Voigt's piezoelectric equations can thus be written in tensor form

$$\begin{aligned} S_{ij} &= s_{ijkl}{}^E T_{kl} + d_{mij} E_m, \\ \sigma_n &= \frac{\epsilon_{mn}{}^T}{4\pi} E_m + d_{nkl} T_{kl}, \end{aligned} \quad (13)$$

where E_m are the three applied fields, σ_n the surface charges normal to the three axes, d_{ijm} the third rank piezoelectric tensor relating the strains to the applied fields or the electric displacement to the applied stresses. In a similar way to the elasticities, the two index piezoelectric symbols are related to the three index symbols if we replace the ij terms

$$\begin{matrix} 1 \text{ by } 11, & 2 \text{ by } 22, & 3 \text{ by } 33, \\ 4 \text{ by } 23, & 5 \text{ by } 13 & \text{and} \quad 6 \text{ by } 12. \end{matrix} \quad (14)$$

For any number 4, 5, or 6, the piezoelectric constant d_{im} has to be divided by 2 to equal the corresponding d_{ijm} constant.

To find the form of the piezoelectric equations for which the electric displacement $D/4\pi$ is the independent variable, the following derivation can be used. Let us first consider the dielectric "impermeability" tensor $\beta_{mn}{}^T$ which is formed from the dielectric constant tensor $\epsilon_{mn}{}^T$ by means of the relation

$$\beta_{mn}{}^T = (-1)^{(m+n)} \Delta\epsilon_{mn}{}^T / \epsilon_{mn}{}^T, \quad (15)$$

where $\epsilon_{mn}{}^T$ is the dielectric constant tensor

$$\begin{vmatrix} \epsilon_{11}{}^T, & \epsilon_{12}{}^T, & \epsilon_{13}{}^T \\ \epsilon_{12}{}^T, & \epsilon_{22}{}^T, & \epsilon_{23}{}^T \\ \epsilon_{13}{}^T, & \epsilon_{23}{}^T, & \epsilon_{33}{}^T \end{vmatrix} \quad (16)$$

and $\Delta\epsilon_{mn}{}^T$ is the determinant formed from this tensor by suppressing the mth row and nth column. We next multiply both sides of the last of Eq. (13) by $4\pi\beta_{mn}{}^T$ giving

$$4\pi\beta_{mn}{}^T \sigma_n = E_m[\beta_{mn}{}^T \epsilon_{mn}{}^T] + 4\pi\beta_{mn}{}^T d_{nkl} T_{kl}. \quad (17)$$

If we take the product $\epsilon_{mn}{}^T \beta_{mn}{}^T$ for the three values of m, we have as the multipliers of E_1, E_2, E_3, respectively,

$$\begin{aligned} &\epsilon_{11}{}^T \beta_{11}{}^T + \epsilon_{12}{}^T \beta_{12}{}^T + \epsilon_{13}{}^T \beta_{13}{}^T, \\ &\epsilon_{21}{}^T \beta_{21}{}^T + \epsilon_{22}{}^T \beta_{22}{}^T + \epsilon_{23}{}^T \beta_{23}{}^T, \\ &\epsilon_{31}{}^T \beta\pi_1{}^T + \epsilon_{32}{}^T \beta_{32}{}^T + \epsilon_{33}{}^T \beta_{33}{}^T. \end{aligned} \quad (18)$$

But by virtue of the definition of $\beta_{mn}{}^T$ given by Eq. (15) it is obvious that the value of each term is unity so that Eq. (17) can be written

$$\begin{aligned} E_m &= 4\pi\beta_{mn}{}^T \sigma_n - 4\pi\beta_{mn}{}^T d_{nkl} T_{kl} \\ &= 4\pi\beta_{mn}{}^T \sigma_n - g_{mkl} T_{kl}, \end{aligned} \quad (19)$$

where the new piezoelectric constants g_{mkl} relating the fields to the applied forces or the strains to the electric displacement is given in terms of the d_{nkl} piezoelectric constants and the "free" dielectric impermeability by the tensor equation

$$g_{mkl} = 4\pi\beta_{mn}{}^T d_{nkl}. \quad (20)$$

Introducing the value of E_m into the first of Eqs. (13) we find

$$S_{ij} = s_{ijkl}{}^D T_{kl} + g_{mij} \sigma_n, \quad (21)$$

where the open circuit or zero charge elastic compliances are given by

$$s_{ijkl}{}^D = s_{ijkl}{}^E - d_{mij} g_{mkl}. \quad (22)$$

Hence the complete piezoelectric equation can be written

$$\begin{aligned} S_{ij} &= s_{ijkl}{}^D T_{kl} + g_{mij} \sigma_n, \\ E_m &= 4\pi\beta_{mn}{}^T \sigma_n - g_{mkl} T_{kl}. \end{aligned} \quad (23)$$

III. Equations of Motion of a Piezoelectric Crystal

The equation of motion of a piezoelectric crystal or any aeolotropic body can be derived from Newton's laws of motion and the piezoelectric Eqs. (13). Newton's law can be written in the tensor form

$$\rho \frac{\partial^2 \xi_k}{\partial t^2} dx_1 dx_2 dx_3 = F_k, \quad (24)$$

where ξ_k are the displacements of the elementary cube $dx_1dx_2dx_3$ in the x_1, x_2, x_3 directions, F_k are the components of force in these directions exerted on the elementary cube, and ρ is the density of the material within the cube. From elastic theory we have that the total resultant force along the x_1 direction is the partial derivatives of the stresses in this direction or

$$F_1 = +\left[\frac{\partial T_{11}}{\partial x_1}+\frac{\partial T_{12}}{\partial x_2}+\frac{\partial T_{13}}{\partial x_3}\right]dx_1dx_2dx_3 = +\frac{\partial T_{1l}}{\partial x_l}dx_l. \tag{25}$$

For the forces in any direction we can write the general tensor relations

$$F_k = +\frac{\partial T_{kl}}{\partial x_l}dx_l. \tag{26}$$

Hence the equations of motion become

$$\rho\frac{\partial^2 \xi_k}{\partial t^2} = +\frac{\partial T_{kl}}{\partial x_l}. \tag{27}$$

Into this equation we can insert expressions for the strains in terms of the stresses and applied charges and obtain the partial differential equations for any mode of motion. However, before doing this it is desirable to discuss the boundary condition that such crystals have to satisfy.

The elastic conditions for a crystal free to vibrate are that the stresses normal to the free edges are zero. For a surface whose normal has the direction cosines l_1, l_2, l_3 with respect to the X_1, X_2, X_3 axes, respectively, the conditions reduce to

$$\begin{aligned} T_x &= T_{11}l_1+T_{12}l_2+T_{13}l_3 = T_{1j}l_j = 0, \\ T_y &= T_{21}l_1+T_{22}l_2+T_{23}l_3 = T_{2j}l_j = 0, \\ T_z &= T_{31}l_1+T_{32}l_2+T_{33}l_3 = T_{3j}l_j = 0, \end{aligned} \tag{28}$$

where T_x, T_y, and T_z are the stresses along the X_1, X_2, X_3 axes. If we denote these by T_i, the boundary conditions can be abbreviated into

$$T_i = T_{ij}l_j = 0. \tag{29}$$

The electrical boundary conditions are determined by whether plating is placed on the surface of the crystal or not. If any plating is a long distance from the crystal, then the surface charge σ_i is necessarily zero since no path exists for conducting charge to this surface. If, on the other hand, a plating is integral with the surface normal to the x_1 axis, the surface charge σ_1 will not be zero but will be a function of the other two directions x_2 and x_3. In the interior of the crystal, the electrical condition is expressed by determining the electrical induction D. At every point of the interior the divergence of the electric induction vector is equal to zero, or

$$\frac{\partial D_1}{\partial x_1}+\frac{\partial D_2}{\partial x_2}+\frac{\partial D_3}{\partial x_3} = \frac{\partial D_i}{\partial x_i} = 0. \tag{30}$$

At the surface of the crystal the normal component of the electric induction divided by 4π is equal to the surface charge. At the plated surface the electric field starts out normal to the surface since the tangential components of the field on crossing a boundary are continuous, and for a plated surface the tangential component of the field is zero. These equations are sufficient to determine the electrical as well as the mechanical reactions of the crystal.

IV. Equation for Simple Longitudinal Vibrations

In obtaining the elastic and piezoelectric constants of a crystal, it is necessary to vibrate the crystal in a simple mode of motion and determine the constants from the measured resonant and anti-resonant frequencies, and the capacities of the crystal. The simplest mode of motion and the one most easily related to the elastic constants is the simple longitudinal mode of motion. If we take x_1 as the thickness direction and apply plating to these surfaces of the crystal, the only value of surface charge different from zero will be σ_1 since no electrical connection is made to the other surfaces. Since x_1 is assumed small, the voltage gradient $\partial E_1/\partial x_1$ will be a constant throughout the thickness of the crystal. Also, since the plating is an equipotential surface

$$\frac{\partial E_1}{\partial x_2} = \frac{\partial E_1}{\partial x_3} = 0. \tag{31}$$

We take the length along the x_2 axis and the width along the x_3 axis. For sides normal to the thickness, the boundary conditions are

$$T_{11}=T_{12}=T_{13}=0. \tag{32}$$

Since the thickness is taken as small and all the stresses are zero on the two surfaces normal to x_1, these stresses cannot differ appreciably from zero in the interior and hence we can set

$$T_{11}=T_{12}=T_{13}=0 \tag{32}$$

for all elements of the crystal. Similarly since the width is considered very small, the stresses

$$T_{31}=T_{32}=T_{33}=0. \tag{33}$$

For the length, the only finite dimension, the stresses on the surface are

$$T_{21},\ T_{22},\ T_{23}. \tag{34}$$

Of these $T_{21}=T_{12}$ and $T_{23}=T_{32}$ have already been found to be zero so that the only stress different from zero in the interior is T_{22}.

Inserting this condition in Eq. (27) the only equation of motion resulting is

$$\rho\frac{\partial^2\xi_2}{\partial t^2}=+\frac{\partial T_{22}}{\partial x_2}. \tag{35}$$

Since T_{22} is the only stress, the corresponding strains are given by Eq. (13), first part. For the case of interest here, $k=l=2$ and since a charge is developed only in the x_1 direction, $n=1$. Hence we have

$$S_{ij}=s_{ij22}{}^E T_{22}+d_{lij}E_1. \tag{36}$$

In particular the stress T_{22} can be specified by a single strain, all the other strains being related dependently to this one. Taking the strain S_{22} since it is simply related to the displacement ξ_2, we can write

$$S_{22}=s_{2222}{}^E T_{22}+d_{122}E_1$$

or

$$T_{22}=+\frac{S_{22}}{s_{2222}{}^E}-\frac{d_{122}E_1}{s_{2222}{}^E}. \tag{37}$$

The electrical relations of (13) reduce to the form

$$\sigma_n=4\pi\epsilon_{n_1}{}^T E_1+d_{n22}T_{22}$$

$$=\left(4\pi\epsilon_{n_1}{}^T-\frac{d_{m22}d_{122}}{s_{2222}{}^E}\right)E_1-\frac{d_{n22}}{s_{2222}{}^E}S_{22}. \tag{38}$$

The only charge of interest is the one in the x_1 direction which is the direction of the applied field. Hence

$$\sigma_1=\left[4\pi\epsilon_{11}{}^T-\frac{d_{122}{}^2}{s_{2222}{}^E}\right]E_1+\frac{d_{122}}{s_{2222}{}^E}S_{22}. \tag{39}$$

Finally we call the expression

$$4\pi\epsilon_{11}{}^T-\frac{d_{122}{}^2}{s_{2222}{}^E}=4\pi\epsilon_{11}{}^{LC}=4\pi\epsilon_{11}{}^{S_{22}}, \tag{40}$$

indicating that it is the longitudinally clamped dielectric constant which relates the potential and surface charge when the crystal is clamped so that S_{22} disappears.

In terms of the more usual two index symbols, the two piezoelectric and elastic relations can be written

$$\begin{aligned}\rho\frac{\partial^2\xi_2}{\partial t^2}&=\frac{1}{s_{22}{}^E}\frac{\partial^2\xi_2}{\partial x_2{}^2}-\frac{d_{12}}{s_{22}{}^E}\frac{\partial E_1}{\partial x_2},\\ \sigma_1&=4\pi\epsilon_{11}{}^{LC}E_1-\frac{d_{12}}{s_{22}{}^E}\frac{\partial\xi_2}{\partial x_2}.\end{aligned} \tag{41}$$

To solve this equation we note that E_1 is a constant independent of x_2 since the plating forms an equipotential surface. Hence the equation of motion becomes

$$\rho\frac{\partial^2\xi_2}{\partial t^2}=\frac{1}{s_{22}{}^E}\frac{\partial^2\xi_2}{\partial x_2{}^2}. \tag{42}$$

The equations of motion (41) and (42) have been solved several times in published papers[6] so that only the final results will be given. From this analysis it can be shown that the admittance of the free crystal is

$$\frac{1}{Z}=\frac{i}{E}=\frac{i}{E_1 l_t}$$

$$=\frac{j\omega l_w l\epsilon_{11}{}^{LC}}{4\pi l_t}\left[1+\frac{4\pi d_{12}{}^2}{\epsilon_{11}{}^{LC}s_{22}{}^E}\left(\frac{\tan\omega l/2v}{\omega l/2v}\right)\right]. \tag{43}$$

At very low frequencies this admittance reduces to the capacitance reactance

$$\frac{j\omega l_w l\epsilon_{11}{}^T}{4\pi l_t}=j\omega C_0 \tag{44}$$

---

[6] See W. P. Mason, Phys. Rev. **69**, 173 (1946).

so that the low frequency measurement of the capacitance C_0 determines the "free" dielectric constant ϵ_{11}^T. When the tangent

$$\tan\frac{\omega l}{2v}=\infty \quad\text{or}\quad \frac{\omega l}{2v}=\frac{\pi}{2};$$
$$f_R=\frac{v}{2l}=\frac{1}{2l(\rho s_{22}^E)^{\frac{1}{2}}}. \tag{45}$$

A resonant frequency is obtained whose value is determined by the elastic compliance s_{22}^E, the density ρ, and the length of the crystal.

The anti-resonance occurs when the expressions in brackets in Eq. (43) equals zero or when

$$1+\frac{4\pi d_{12}^2}{\epsilon_{11}^{LC}s_{22}^E}\left(\frac{\tan\omega_A l/2v}{\omega_A l/2v}\right)=0$$

or

$$\frac{\omega_A l}{2v}\cot\frac{\omega_A l}{2v}=-\frac{4\pi d_{12}^2}{\epsilon_{11}^{LC}s_{22}^E}. \tag{46}$$

Defining the coefficient of electromechanical coupling as

$$k=\frac{d_{12}}{\left(\dfrac{\epsilon_{11}^T}{4\pi}s_{22}^E\right)^{\frac{1}{2}}}, \tag{47}$$

and substituting the value of ϵ_{11}^{LC} from Eq. (40) in Eq. (46) this becomes

$$\frac{\omega_A l}{2v}\cot\frac{\omega_A l}{2v}=-\left(\frac{k^2}{1-k^2}\right). \tag{48}$$

We wish now to obtain an expression for evaluating the coupling factor k in terms of the measured resonant and anti-resonant frequencies f_R and f_A. Their difference is usually small so that we can write

$$f_A=f_R+\Delta f;\quad \omega_A=\omega_R+2\pi\Delta f. \tag{49}$$

Inserting this expression in (48) and expanding by the multiple angle formula, we have after solving for k^2

$$k^2=\frac{\pi^2}{4}\frac{\Delta f}{f_R}\left[1+\left(\frac{4-\pi^2}{4}\right)\frac{\Delta f}{f_R}+\left(\frac{\pi^2-4}{4}\right)\left(\frac{\pi^2}{4}\right)\left(\frac{\Delta f}{f_R}\right)^2+\cdots\right]. \tag{50}$$

Hence when the frequency difference between resonance and anti-resonance is measured, the coupling coefficient k can be obtained by substituting in the above formula. Usually the first term is sufficient. Having the coupling, the elastic constant s_{22}^E, which can be calculated from the resonant frequency, and ϵ_{11}^T which is obtained by low frequency capacity measurements, the piezoelectric constant d_{12} can be evaluated. By using these constants for rotated cuts, all the independent elastic constants not involving pure shear, most of the piezoelectric constants, and all of the dielectric constants can be evaluated.

V. Evaluation of Shearing Constants from Face Shear Vibrations

A measurement of various orientations of the crystal in longitudinal vibration will evaluate all of the elastic constants except the shearing constants. To measure the shearing elastic constants requires setting up a vibration in which a pure shear is the predominant motion. A choice can be made of a thickness shear mode or a face shear mode and the latter was chosen since the mode is simpler and is more easily dimensioned and because the fundamental constants can be directly measured by a single orientation. It is the purpose of this section to derive the resonant frequencies of a face shear mode.

This is a more general contour mode than the longitudinal mode considered and involves satisfying boundary conditions along four edges. We consider a crystal cut normal to the Z or X_3 axis and assume that the thickness is so small that the stresses determined by the X_3 direction can be set equal to zero. Hence

$$T_{31}=T_{32}=T_{33}=0. \tag{51}$$

The remaining stresses

$$T_{11},\ T_{12},\ \text{and}\ T_{22} \tag{52}$$

are all finite throughout the crystal but vanish at the edges. The vanishing of the stresses in Eq. (51) simplifies the equations of motion for it results in only three independent strains, i.e., the other three strains have a definite ratio to the independent strains. Since the field E is parallel to the Z axis at the surface, and the thickness is assumed small, the only component of the field will be E_3. Then Eq. (13) can be written

$$\begin{aligned} S_{11}&=S_1=s_{11}{}^ET_1+s_{12}{}^ET_2+s_{16}{}^ET_6+d_{31}E_3,\\ 2S_{12}&=S_6=s_{16}{}^ET_1+s_{26}{}^ET_2+s_{66}{}^ET_6+d_{36}E_3,\\ S_{22}&=S_2=s_{12}{}^ET_1+s_{22}{}^ET_2+s_{26}{}^ET_6+d_{32}E_3,\\ \sigma_3&=\frac{\epsilon_{33}{}^TE_3}{4\pi}+d_{31}T_1+d_{32}T_2+d_{36}T_6. \end{aligned} \tag{53}$$

All the other stresses disappear by virtue of (51)

For inserting in the equations of motion it is desirable to express the stress in terms of the strain. This can be done by solving Eq. (53) simultaneously, giving

$$\begin{aligned} T_1&=c_{11}{}^{c,E}S_1+c_{12}{}^{c,E}S_2+c_{16}{}^{c,E}S_6-e_{31}{}^cE_3,\\ T_2&=c_{12}{}^{c,E}S_1+c_{22}{}^{c.E}S_2+c_{26}{}^{c,E}S_6-e_{32}{}^cE_3,\\ T_6&=c_{16}{}^{c,E}S_1+c_{26}{}^{c,E}S_2+c_{66}{}^{c,E}S_6-e_{36}{}^cE_3,\\ \sigma_3&=E_3\left[\frac{\epsilon_{33}{}^T}{4\pi}-(d_{31}e_{31}{}^c+d_{32}e_{32}{}^c+d_{36}e_{36}{}^c)\right]\\ &\qquad+e_{31}{}^cS_1+e_{32}{}^cS_2+e_{36}{}^cS_6. \end{aligned} \tag{54}$$

In these equations $c_{ij}{}^{c,E}$ designate the field contour elastic constants that apply when a contour mode occurs for a very thin crystal. These constants are given in terms of the elastic compliances at constant field by the formula

$$c_{ij}{}^{c,E}=\frac{(-1)^{k+l}\Delta_{kl}}{\Delta}(k,l=1,2,3), \tag{55}$$

where Δ is the determinant

$$\Delta=\begin{vmatrix} s_{11}{}^E, & s_{12}{}^E, & s_{16}{}^E\\ s_{12}{}^E, & s_{22}{}^E, & s_{26}{}^E\\ s_{16}{}^E, & s_{26}{}^E, & s_{66}{}^E \end{vmatrix}$$

and Δ_{kl} is the minor obtained by suppressing the kth row and lth column. The piezoelectric moduli applying to a contour mode of motion are given by

$$\begin{aligned} e_{31}{}^c&=d_{31}c_{11}{}^{c,E}+d_{32}c_{12}{}^{c,E}+d_{36}c_{16}{}^{c,E},\\ e_{32}{}^c&=d_{31}c_{12}{}^{c,E}+d_{32}c_{22}{}^{c,E}+d_{36}c_{26}{}^{c,E},\\ e_{36}{}^c&=d_{31}c_{16}{}^{c,E}+d_{32}c_{26}{}^{c,E}+d_{36}c_{66}{}^{c,E}, \end{aligned} \tag{56}$$

while the contour clamped dielectric constant is given by the equation

$$\epsilon_{33}{}^{c,S}=\epsilon_{33}{}^T-(d_{31}e_{31}{}^c+d_{32}e_{32}{}^c+d_{36}e_{36}{}^c)4\pi. \tag{57}$$

The superscripts c,S indicate that this is the dielectric constant if the crystal is free from contour strains, but not for thickness modes.

Inserting Eqs. (54) in the equations of motion (27) noting that

$$\partial E_3/\partial x_1=\partial E_3/\partial x_2=0,$$

since the plating is an equipotential surface, the equations of motion become

$$\begin{aligned} \rho\frac{\partial^2\xi_1}{\partial t^2}&=c_{11}{}^{c,E}\frac{\partial^2\xi_1}{\partial x_1{}^2}+2c_{16}{}^{c,E}\frac{\partial^2\xi_1}{\partial x_1\partial x_2}+c_{66}{}^{c,E}\frac{\partial^2\xi_1}{\partial x_2{}^2}+c_{16}{}^{c,E}\frac{\partial^2\xi_2}{\partial x_1{}^2}+(c_{12}{}^{c,E}+c_{66}{}^{c,E})\frac{\partial^2\xi_2}{\partial x_1\partial x_2}+c_{26}{}^{c,E}\frac{\partial^2\xi_2}{\partial x_2{}^2},\\ \rho\frac{\partial^2\xi_2}{\partial t^2}&=c_{16}{}^{c,E}\frac{\partial^2\xi_1}{\partial x_1{}^2}+(c_{12}{}^{c,E}+c_{66}{}^{c,E})\frac{\partial^2\xi_1}{\partial x_1\partial x_2}+c_{26}{}^{c,E}\frac{\partial^2\xi_1}{\partial x_2{}^2}+c_{66}{}^{c,E}\frac{\partial^2\xi_2}{\partial x_1{}^2}+2c_{26}{}^{c,E}\frac{\partial^2\xi_2}{\partial x_1\partial x_2}+c_{22}{}^{c,E}\frac{\partial^2\xi_2}{\partial x_2{}^2}. \end{aligned} \tag{58}$$

For simple harmonic motion, Eqs. (58) reduce to the form

$$\begin{aligned} &c_{11}\frac{\partial^2\xi_1}{\partial x_1{}^2}+2c_{16}\frac{\partial^2\xi_1}{\partial x_1\partial x_2}+c_{66}\frac{\partial^2\xi_1}{\partial x_2{}^2}+c_{16}\frac{\partial^2\xi_2}{\partial x_1{}^2}+(c_{12}+c_{66})\frac{\partial^2\xi_2}{\partial x_1\partial x_2}+c_{26}\frac{\partial^2\xi_2}{\partial x_2{}^2}+\omega^2\rho\xi_1=0,\\ &c_{16}\frac{\partial^2\xi_1}{\partial x_1{}^2}+(c_{12}+c_{66})\frac{\partial^2\xi_1}{\partial x_1\partial x_2}+c_{26}\frac{\partial^2\xi_1}{\partial x_2{}^2}+c_{66}\frac{\partial^2\xi_2}{\partial x_1{}^2}+2c_{26}\frac{\partial^2\xi_2}{\partial x_1\partial x_2}+c_{22}\frac{\partial^2\xi_2}{\partial x_2{}^2}+\omega\rho\xi_2=0, \end{aligned} \tag{59}$$

where the elastic constants are understood to be the contour, potential constants.

For experimental purposes it is found that the best measurements are obtained when the crystal is long compared to its width or thickness. This is further accentuated by taking a high harmonic of this mode which in effect makes the unit cell longer compared to its width. Hence the solution of interest is one where the crystal is infinitely long in the x_1 direction and with a finite width in the x_2 direction. For the infinitely long crystal, there should be no variation of the displacements ξ_1 or ξ_2 along the length of the crystal and hence

$$\frac{\partial^2\xi_1}{\partial x_1}=\frac{\partial^2\xi_1}{\partial x_1\partial x_2}=\frac{\partial^2\xi_2}{\partial x_1^2}=\frac{\partial^2\xi_2}{\partial x_1\partial x_2}=0 \tag{60}$$

this leaves only the terms

$$c_{66}\frac{\partial^2\xi_1}{\partial x_2^2}+c_{26}\frac{\partial^2\xi_2}{\partial x_2^2}+\omega^2\rho\xi_1=0,\quad c_{26}\frac{\partial^2\xi_1}{\partial x_2^2}+c_{22}\frac{\partial^2\xi_2}{\partial x_2^2}+\omega^2\rho\xi_2=0. \tag{61}$$

The solution of these equations represents two coupled motions controlled by the x_2 dimension. If $c_{26}=0$ these two motions are a shear vibration and a longitudinal vibration existing independently, but with c_{26} finite, the shear and the longitudinal motions are coupled so that there is no pure shear or pure longitudinal motion. To show this we can eliminate ξ_2 from the above equation and obtain one fourth-order equation

$$\frac{\partial^4\xi_1}{\partial x_2^4}+\omega^2\rho\left[\frac{c_{22}+c_{66}}{c_{22}c_{66}-c_{66}^2}\right]\frac{\partial^2\xi_2}{\partial x_2^2}+\frac{\omega^4\rho^2\xi_1}{c_{22}c_{66}-c_{26}^2}=0. \tag{62}$$

A solution of this equation is

$$\xi_1=A\cos\alpha x_2+B\sin\alpha x_2+C\cos\beta x_2+D\sin\beta x_2,$$

where

$$\begin{aligned}\alpha&=\omega\left(\frac{(c_{22}+c_{66})\rho}{2(c_{22}c_{66}-c_{26}^2)}\right)^{\frac{1}{2}}\left(1+\left[\frac{(c_{22}-c_{66})^2+4c_{26}^2}{(c_{22}+c_{66})^2}\right]^{\frac{1}{2}}\right)^{\frac{1}{2}},\\ \beta&=\omega\left(\frac{(c_{22}+c_{66})\rho}{(c_{22}c_{66}-c_{26}^2)}\right)^{\frac{1}{2}}\left(1-\left[\frac{(c_{22}-c_{66})^2+4c_{26}^2}{(c_{22}+c_{66})^2}\right]^{\frac{1}{2}}\right)^{\frac{1}{2}}.\end{aligned} \tag{63}$$

If $c_{26}=0$

$$\alpha=\omega(\rho/c_{66})^{\frac{1}{2}};\quad \beta=\omega(\rho/c_{22})^{\frac{1}{2}},$$

and the two vibrations would exist independently.

The value of ξ_2 is obtained by a substitution of the value of ξ_1 in the last of Eq. (61) and is

$$\xi_2=\left(\frac{\alpha^2c_{26}}{\omega^2\rho-\alpha^2c_{22}}\right)[A\cos\alpha x_2+B\sin\alpha x_2]+\left(\frac{\beta^2c_{26}}{\omega^2\rho-\beta^2c_{22}}\right)[C\cos\beta x_2+D\sin\beta x_2]. \tag{64}$$

The boundary conditions to be satisfied are

$$\begin{aligned}T_2&=c_{22}\frac{\partial\xi_2}{\partial x_2}+c_{26}\frac{\partial\xi_1}{\partial x_2}-e_{31}{}^cE_3=0\quad\text{when}\quad x_2=0\quad\text{and}\quad x_2=l_w,\\ T_6&=c_{26}\frac{\partial\xi_2}{\partial x_2}+c_{66}\frac{\partial\xi_1}{\partial x_2}-e_{36}{}^cE_3=0\quad\text{when}\quad x_2=0\quad\text{and}\quad x_2=l_w,\end{aligned} \tag{65}$$

where l_w is the width of the crystal. These conditions determine the four independent constants A,

B, C, and D. In terms of E_3 these constants are

$$
\begin{aligned}
A&=-\left[\frac{(\omega^2\rho-\alpha^2c_{22})\tan\alpha l_w/2}{\alpha[\beta^2-\alpha^2][c_{22}c_{66}-c_{26}{}^2]}\right]\left[e_{36}{}^cE_3-e_{32}{}^cE_3\left[\frac{\omega^2\rho c_{66}-\beta^2(c_{22}c_{66}-c_{26}{}^2)}{\omega^2\rho c_{26}}\right]\right],\\
B&=\left[\frac{(\omega^2\rho-\alpha^2c_{22})}{\alpha[\beta^2-\alpha^2][c_{22}c_{66}-c_{26}{}^2]}\right]\left[e_{36}{}^cE_3-e_{32}{}^cE_3\left[\frac{\omega^2\rho c_{66}-\beta^2(c_{22}c_{66}-c_{26}{}^2)}{\omega^2\rho c_{26}}\right]\right],\\
C&=\left[\frac{(\omega^2\rho-\beta^2c_{22})\tan\beta l_w/2}{\beta(\beta^2-\alpha^2)(c_{22}c_{66}-c_{26}{}^2)}\right]\left[e_{36}{}^cE_3-e_{32}{}^cE_3\left[\frac{\omega^2\rho c_{66}-\alpha^2(c_{22}c_{66}-c_{26}{}^2)}{\omega^2\rho c_{26}}\right]\right],\\
D&=-\left[\frac{(\omega^2\rho-\beta^2c_{22})}{\beta(\beta^2-\alpha^2)(c_{22}c_{66}-c_{26}{}^2)}\right]\left[e_{36}{}^cE_3-e_{32}{}^cE_3\left[\frac{\omega^2\rho c_{66}-\alpha^2(c_{22}c_{66}-c_{26}{}^2)}{\omega^2\rho c_{26}}\right]\right].
\end{aligned}
\tag{66}
$$

To obtain the electrical admittance of the crystal, we make use of the last of Eqs. (54) which for this limiting case becomes

$$\sigma_3=\frac{E_3\epsilon_3{}^{c,S}}{4\pi}+e_{32}{}^c\frac{\partial\xi_2}{\partial x_2}+e_{36}{}^c\frac{\partial\xi_1}{\partial x_2}. \tag{67}$$

Integrating this equation over the length and width, noting that E_3 does not vary over the surface and ξ_2 and ξ_1 are not functions of x_1, we have

$$Q=\frac{E_3l_wl\epsilon_3{}^{c,S}}{4\pi}+e_{32}{}^cl[\xi_{22}-\xi_{21}]+e_{36}{}^cl[\xi_{12}-\xi_{11}] \tag{68}$$

where the displacements are the displacements at the two edges, and Q is the total charge on the surface. Introducing the displacements from Eq. (63), (64), and (66) and noting that the current to enter the crystal is $j\omega Q$, the admittance of the crystal becomes

$$
\begin{aligned}
\frac{i}{E}=\frac{j\omega ll_w\epsilon_{33}{}^{c,S}}{4\pi l_t}\Bigg[1-\frac{e_{32}{}^24\pi}{\epsilon_{33}{}^{c,S}}\Bigg[\frac{\alpha^2[\omega^2\rho c_{66}-\beta^2(c_{22}c_{66}-c_{26}{}^2)]}{(\beta^2-\alpha^2)(c_{22}c_{66}-c_{26}{}^2)\omega^2\rho}\left(\frac{\tan\alpha l_w/2}{\alpha l_w/2}\right)\\
-\frac{\beta^2[\omega^2\rho c_{66}-\alpha^2(c_{22}c_{66}-c_{26}{}^2)]}{[(\beta^2-\alpha^2)(c_{22}c_{66}-c_{26}{}^2)\omega^2\rho]}\times\frac{\tan\beta l_w/2}{\beta l_w/2}\Bigg]+\frac{4\pi e_{36}{}^2}{\epsilon_{33}{}^{c,S}}\Bigg[\Bigg[\frac{(\omega^2\rho-\alpha^2c_{22})\left(\dfrac{\tan\alpha l_w/2}{\alpha l_w/2}\right)}{(\beta^2-\alpha^2)(c_{22}c_{66}-c_{26}{}^2)}\Bigg]\\
-\Bigg[\frac{(\omega^2\rho-\beta^2c_{22})\left(\dfrac{\tan\beta l_w/2}{\beta l_w/2}\right)}{(\beta^2-\alpha^2)(c_{22}c_{66}-c_{26}{}^2)}\Bigg]\Bigg]-\frac{4\pi e_{32}e_{36}}{\epsilon_{33}{}^{c,S}}\Bigg[\Bigg[\frac{c_{66}(\omega^2\rho-\alpha^2c_{22})(\omega^2\rho-\beta^2c_{22})-\alpha^2\beta^2c_{22}c_{26}{}^2}{(\beta^2-\alpha^2)(c_{22}c_{66}-c_{26}{}^2)\omega_2\rho c_{26}}\Bigg]\\
\times\left[\frac{\tan\alpha l_w/2}{\alpha l_w/2}-\frac{\tan\beta l_w/2}{\beta l_w/2}\right]+\left(\frac{c_{26}}{c_{22}c_{66}-c_{26}{}^2}\right)\left[\frac{\tan\alpha l_w/2}{\alpha l_w/2}+\frac{\tan\beta l_w/2}{\beta l_w/2}\right]\Bigg]\Bigg]\Bigg].
\end{aligned}
\tag{69}
$$

At low frequencies

$$\frac{\tan\alpha l_w}{\alpha l_w/2}\rightarrow\frac{\tan\beta l_w/2}{\beta l_w/2}\rightarrow 1, \tag{70}$$

and the admittance is a capacity

$$C=\frac{ll_w\epsilon_{33}{}^{c,S}}{4\pi l_t}\left[1+\frac{4\pi e_{32}{}^2}{\epsilon_{33}{}^{c,S}}\left[\frac{c_{66}}{c_{22}c_{66}-c_{26}{}^2}\right]+\frac{4\pi e_{36}{}^2}{\epsilon_{33}{}^{c,S}}\left[\frac{c_{22}}{c_{22}c_{66}-c_{26}{}^2}\right]-\frac{4\pi e_{32}e_{36}}{\epsilon_{33}{}^{c,S}}\left(\frac{2c_{26}}{c_{22}c_{66}-c_{26}{}^2}\right)\right]. \tag{71}$$

This capacitance is the "free" dielectric capacitance.

If $c_{26}=0$, the impedance reduces to that for two uncoupled modes, and is

$$\frac{i}{E}=\frac{j\omega ll_w\epsilon_{33}{}^{c,S}}{4\pi l_t}\left\{1+\frac{4\pi e_{32}{}^2}{\epsilon_{33}{}^{c,S}c_{22}}\left[\frac{\tan\omega\left(\frac{\rho}{c_{22}}\right)^{\frac{1}{2}}\frac{l_w}{2}}{\omega\left(\frac{\rho}{c_{22}}\right)^{\frac{1}{2}}\frac{l_w}{2}}\right]+\frac{4\pi e_{32}{}^2}{\epsilon_{33}{}^{c,S}}\left[\frac{\tan\omega\left(\frac{\rho}{c_{22}}\right)^{\frac{1}{2}}\frac{l_w}{2}}{\omega\left(\frac{\rho}{c_{22}}\right)^{\frac{1}{2}}\frac{l_w}{2}}\right]\right\}. \tag{72}$$

For the general case where c_{26} is not zero, Eq. (69) is the admittance of two coupled modes. The resonant frequencies occur when the admittance is infinite (impedance zero) and hence occur when

$$\tan\alpha l_w/2=\infty \quad\text{or}\quad \tan\beta l_w/2=\infty. \tag{73}$$

These are satisfied for the first modes when

$$\begin{aligned}f_1&=\frac{1}{2l_w}\left(\frac{(c_{22}+c_{66})-[(c_{22}-c_{66})^2+4c_{26}{}^2]^{\frac{1}{2}}}{2\rho}\right)^{\frac{1}{2}},\\ f_2&=\frac{1}{2l_w}\left(\frac{(c_{22}+c_{66})+[(c_{22}-c_{66})^2+4c_{26}{}^2]^{\frac{1}{2}}}{2\rho}\right)^{\frac{1}{2}}.\end{aligned} \tag{74}$$

Since the frequency f is equal to the velocity of propagation $v/2l_w$, we find that the two values of the velocity satisfy the determinant

$$\begin{vmatrix}\rho v^2-c_{22}, & c_{26}\\ c_{26}, & \rho v^2-c_{66}\end{vmatrix}=0. \tag{75}$$

VI. Elastic, Piezoelectric, and Dielectric Constants of Rotated Crystals

We have so far calculated the resonant and anti-resonant frequencies of longitudinal crystals cut normal to the X or X_1 axis of the crystal and with the length along the Y or X_2 axis, and the frequencies of a face shear mode cut normal to the Z or X_3 axis with the width (frequency controlling dimension) along the Y or X_2 axis. To measure all the properties of a crystal requires a number of different orientations for both longitudinal and shear vibrations. To make the solutions given previously hold for any of these oriented crystals, we use a system of rotated axes which are rotated from the reference axes by three rotations for the most general case.

Starting with the reference axes, the elastic constants for any rotated cuts are given by the general tensor formula

$$s_{ijkl}'=\frac{\partial x_i'}{\partial x_m}\frac{\partial x_j'}{\partial x_n}\frac{\partial x_k'}{\partial x_o}\frac{\partial x_l'}{\partial x_p}s_{mnop}, \tag{76}$$

where the partial derivatives are the direction cosines defined by Eq. (4). In a similar manner, the peizoelectric and dielectric tensors are given by the formulae

$$d_{ijk}'=\frac{\partial x_i'}{\partial x_l}\frac{\partial x_j'}{\partial x_m}\frac{\partial x_k'}{\partial x_n}d_{lmn}, \tag{77}$$

$$\epsilon_{ij}'=\frac{\partial x_i'}{\partial x_k}\frac{\partial x_j'}{\partial x_l}\epsilon_{kl}. \tag{78}$$

For a monoclinic crystal, with the Y axis taken as the axis of twofold symmetry, the three tensors have the form shown below when the axes chosen are the X, Y, and Z axes as defined in the text

$$\epsilon_{kl}=\begin{vmatrix}\epsilon_{11}, & 0, & \epsilon_{13}\\ 0, & \epsilon_{22}, & 0\\ \epsilon_{13}, & 0, & \epsilon_{33}\end{vmatrix}, \qquad (79)$$

$$d_{lmn}=\begin{vmatrix}0, & 0, & 0, & d_{123}, & 0, & d_{112}\\ d_{211}, & d_{222}, & d_{233}, & 0, & d_{213}, & 0\\ 0, & 0, & 0, & d_{323}, & 0, & d_{312}\end{vmatrix}. \qquad (80)$$

Here the first number denotes the direction of the field and the last two numbers the resulting strain. The elastic tensor has the form

$$s_{mnop}=\begin{vmatrix}s_{1111}, & s_{1122}, & s_{1133}, & 0, & s_{1113}, & 0,\\ s_{1122}, & s_{2222}, & s_{2233}, & 0, & s_{2213}, & 0,\\ s_{1133}, & s_{2233}, & s_{3333}, & 0, & s_{3313}, & 0,\\ 0, & 0, & 0, & s_{2323}, & 0, & s_{2312}\\ s_{1113}, & s_{2213}, & s_{3313}, & 0, & s_{1313}, & 0,\\ 0, & 0, & 0, & s_{2312}, & 0, & s_{1212}\end{vmatrix}. \qquad (81)$$

For longitudinal crystals the rotated elastic constant of interest is the s_{2222}' constant since this is the inverse of Young's modulus along the length Y' or X_2'. The piezoelectric constant driving this mode is d_{122}'. Introducing the tensor terms is the tensor Eq. (76), the rotated constant s_{2222}' becomes

$$s_{2222}'=\frac{\partial x_2'}{\partial x_m}\frac{\partial x_2'}{\partial x_n}\frac{\partial x_2'}{\partial x_o}\frac{\partial x_2'}{\partial x_p}s_{mnop}=l_2^4s_{1111}+l_2^2m_2^2(2s_{1122}+4s_{1212})+l_2^2n_2^2(2s_{1133}+4s_{1313})+4l_2^3n_2s_{1113}$$
$$+m_2^4s_{2222}+m_2^2n_2^2(2s_{2233}+4s_{2323})+4n_2^3l_2s_{3313}+n_2^4s_{3333}+m_2^2l_2n_2[4s_{2213}+4s_{2312}]. \qquad (82)$$

In terms of the equivalent two index symbols the equation becomes

$$s_{22}'=l_2^4s_{11}+l_2^2m_2^2(2s_{12}+s_{66})+l_2^2n_2^2(2s_{13}+s_{55})+2l_2^3n_2s_{15}+m_2^4s_{22}+m_2^2n_2^2(2s_{23}+s_{44})+2n_2^3l_2s_{35}$$
$$+n_2^4s_{33}+m_2^2l_2n_2[2s_{25}+s_{46}]. \qquad (83)$$

Hence by cutting nine oriented longitudinally vibrating crystals five elastic constants can be determined and four relations obtained between the other eight elastic constants. Eight of these cuts can be obtained by having the length in the YZ, ZX, and XY planes. For a crystal cut with its length in the YZ plane, with the angle measured from Y equal to θ, we have

$$l_2=0, \quad m_2=\cos\theta, \quad n_2=\sin\theta,$$

hence

$$s_{22}'=s_{22}\cos^4\theta+(2s_{23}+s_{44})\sin^2\theta\cos^2\theta+s_{33}\sin^4\theta(YZ\text{ plane}). \qquad (84)$$

For the XY plane, measuring the length from Y

$$l_2=\sin\varphi, \quad m_2=\cos\varphi, \quad n_2=0,$$

and

$$s_{22}'=s_{22}\cos^4\varphi+(2s_{12}+s_{66})\sin^2\varphi\cos^2\varphi+s_{11}\sin^4\varphi(XY\text{ plane}). \qquad (85)$$

For the ZX plane with ψ measured from positive Z in the direction of positive X, as defined in the text, $l_2=\sin\psi$, $n_2=\cos\psi$, $m_2=0$, and

$$s_{33}'=s_{33}\cos^4\psi+2\cos^3\psi\sin\psi\, s_{35}+\sin^2\psi\cos^2\psi(2s_{13}+s_{55})+2\sin^3\psi\cos\psi\, s_{15}+\sin^4\psi\, s_{11}. \qquad (86)$$

Three crystals each in the YZ plane and XY plane and five in the XZ plane will determine eight relations and give three checks between the constants s_{11}, s_{22}, and s_{33}. To determine the ninth relation requires a crystal with a double orientation and for this purpose the crystal shown by Fig. 9 was used. In this case $l_2=0.5$, $m_2=-0.707$; $n_2=0.5$ and

$$s_{22}'=\tfrac{1}{16}[s_{11}+s_{55}+s_{33}]+\tfrac{1}{8}[s_{13}+s_{15}+s_{44}+s_{35}+s_{66}+s_{46}]+\tfrac{1}{4}[s_{12}+s_{22}+s_{23}+s_{25}]. \qquad (87)$$

The piezoelectric constant for driving these longitudinal crystals, d_{122}' is given in terms of the developed tensor equation

$$d_{122}'=\frac{\partial x_1'}{\partial x_l}\frac{\partial x_2'}{\partial x_m}\frac{\partial x_2'}{\partial x_n}d_{lmn}=2\frac{\partial x_1'}{\partial x_1}\frac{\partial x_2'}{\partial x_2}\frac{\partial x_2'}{\partial x_3}d_{123}+2\frac{\partial x_1'}{\partial x_1}\frac{\partial x_2'}{\partial x_1}\frac{\partial x_2'}{\partial x_2}d_{112}+\frac{\partial x_1'}{\partial x_2}\left(\frac{\partial x_2'}{\partial x_1}\right)^2 d_{211}+\frac{\partial x_1'}{\partial x_2}\left(\frac{\partial x_2'}{\partial x_2}\right)^2 d_{222}$$

$$+\frac{\partial x_1'}{\partial x_2}\left(\frac{\partial x_2'}{\partial x_3}\right)^2 d_{233}+2\frac{\partial x_1'}{\partial x_2}\frac{\partial x_2'}{\partial x_1}\frac{\partial x_2'}{\partial x_3}d_{213}+2\frac{\partial x_1'}{\partial x_3}\frac{\partial x_2'}{\partial x_2}\frac{\partial x_2'}{\partial x_3}d_{323}+2\frac{\partial x_1'}{\partial x_3}\frac{\partial x_2'}{\partial x_1}\frac{\partial x_2'}{\partial x_2}d_{312}. \quad (88)$$

In terms of the two index symbols and the direction cosines this equation becomes

$$d_{12}'=l_1m_2n_2d_{14}+l_1l_2m_2d_{16}+m_1l_2^2d_{21}+m_1m_2^2d_{22}$$
$$+m_1n_2^2d_{23}+m_1l_2n_2d_{25}+n_1m_2n_2d_{34}$$
$$+n_1l_2m_2d_{36}. \quad (89)$$

For crystals cut in the YZ plane with the thickness in the X_1 direction, the direction cosines are

$$\begin{vmatrix} l_1=1, & m_1=0, & n_1=0 \\ l_2=0, & m_2=\cos 0, & n_2=\sin\theta \\ l_3=0, & m_3=-\sin\theta, & n_3=\cos\theta \end{vmatrix} \quad (90)$$

and the piezoelectric constants driving this mode are

$$d_{12}'=d_{14}\sin\theta\cos\theta=\frac{d_{14}}{2}\sin 2\theta. \quad (91)$$

Hence a measurement of the 45° X cut crystal will determine the piezoelectric constant d_{14}. Its sign can be determined from polarity tests. For the XY plane with the thickness along $Z=X_3$, the direction cosines become

$$\begin{vmatrix} l_1=0; & m_1=0; & n_1=-1 \\ l_2=\cos\varphi; & m_2=\sin\varphi; & n_2=0 \\ l_3=-\sin\varphi; & m_3=+\cos\varphi; & n_3=0 \end{vmatrix} \quad (92)$$

and the piezoelectric constant driving this mode is

$$d_{12}'=-d_{36}\sin\varphi\cos\varphi=-\frac{d_{36}}{2}\sin 2\varphi. \quad (93)$$

In the XZ plane with the thickness along the Y axis, the direction cosines are

$$\begin{vmatrix} l_1=0; & m_1=1; & n_1=0 \\ l_2=\sin\psi; & m_2=0; & n_2=\cos\psi \\ l_3=\cos\psi; & m_3=0; & n_3=-\sin\psi \end{vmatrix} \quad (94)$$

and the piezoelectric constant driving this mode is

$$d_{12}'=d_{21}\sin^2\psi+d_{23}\cos^2\psi+\frac{d_{25}}{2}\sin 2\psi. \quad (95)$$

Two more single angle orientations, which will give information on the piezoelectric constants but not on the elastic constants are orientations for which the length and thickness axes both lie in the YZ and XZ planes, respectively. For the first case with the angle θ measured between the length and the Y axis, the direction cosines are

$$\begin{vmatrix} l_1=0; & m_1=\sin\theta; & n_1=-\cos\theta \\ l_2=0; & m_2=\cos\theta; & n_2=\sin\theta \\ l_3=1; & m_3=0; & n_3=0 \end{vmatrix} \quad (96)$$

and the piezoelectric constant d_{12}' is

$$d_{12}'=\sin\theta[(d_{22}-d_{34})\cos^2\theta+d_{23}\sin^2\theta]. \quad (97)$$

Hence if a crystal is cut with its length 45° between the Y and Z axis and its width along the X axis, the piezoelectric constants $(d_{22}-d_{34})$ can be evaluated and compared in sign with d_{23}, which has already been determined from Eq. (95). The second orientation with the length and thickness in the XY plane and with the width along the Z axis, the direction cosines are

$$\begin{vmatrix} l_1=\sin\varphi; & m_1=-\cos\varphi; & n_1=0 \\ l_2=\cos\varphi; & m_2=\sin\varphi; & n_2=0 \\ l_3=0; & m_3=0; & n_3=1 \end{vmatrix} \quad (98)$$

and the piezoelectric constant d_{12}' is given by

$$d_{12}'=-\cos\varphi[d_{21}\cos^2\varphi+(d_{22}-d_{16})\sin^2\varphi]. \quad (99)$$

Hence a crystal cut at 45° between the X and Y axes and with its width along the Z axis will determine the value of $(d_{22}-d_{16})$ since d_{21} is already known.

A check on the piezoelectric constants and their signs is obtained by using one double orientation crystal. The one selected on account of the ease of cutting is the one shown by Fig. 9. From the figure it is readily shown that the direction cosines are

$$\begin{vmatrix} l_1=0.707\sin\theta; & m_1=\cos\theta; & n_1=0.707\sin\theta \\ l_2=0.707\cos\theta; & m_2=-\sin\theta; & n_2=0.707\cos\theta \\ l_3=0.707; & m_3=0; & n_3=-0.707 \end{vmatrix}. \tag{100}$$

With these values the piezoelectric constant for driving this mode is

$$d_{12}'=\frac{(d_{21}+d_{23}+d_{25})}{2}\cos^3\theta + \left[d_{22}-\frac{(d_{14}+d_{16}+d_{34}+d_{36})}{2}\right]\sin^2\theta\cos\theta. \tag{101}$$

Hence by taking $\theta=45°$ this becomes

$$d_{12}'=0.1768[d_{21}+d_{23}+d_{25}] +0.1768[2d_{22}-(d_{14}+d_{16}+d_{34}+d_{36})]. \tag{102}$$

To separate d_{22} from d_{16} and d_{34} requires the measurement of one thickness vibration crystal. The one chosen for DKT was a crystal cut normal to Z, which gave an S_4 shear. This determined the constant d_{34}. From this all the values can be calculated.

To evaluate the shear elastic constants, four crystal cuts are made all of which vibrate in the face shear mode. Three of these are cut normal to the X, Y, and Z axes, respectively, with their width (the frequency determining dimension) along the Z, X, and Y axes, respectively. The fourth cut is made with the thickness direction halfway between the X and Z axes and the width along the Y axis. The frequency of a Z cut crystal has been discussed at some length in Section V and since s_{26} is zero for a monoclinic crystal the shear vibration frequency is determined by

$$f=\frac{1}{2l_w}\left(\frac{c_{66}{}^{c,E}}{\rho}\right)^{\frac{1}{2}}. \tag{103}$$

Then since

$$c_{66}{}^{c,E}=\begin{vmatrix} s_{11}{}^E, & s_{12}{}^E \\ s_{12}{}^E, & s_{22}{}^E \end{vmatrix} \Bigg/ \begin{vmatrix} s_{11}{}^E & s_{12}{}^E & 0 \\ s_{12}{}^E & s_{22}{}^E & 0 \\ 0 & 0 & s_{66}{}^E \end{vmatrix} =\frac{1}{s_{66}{}^E}, \tag{104}$$

the fundamental elastic constant $s_{66}{}^E$ can be evaluated from the measurements.

The frequency of an X cut crystal with its width along Z can in a similar manner be determined since it can be shown that the mode of motion is a simple shear, and the frequency is given by

$$f=\frac{1}{2l_w}\left(\frac{c_{44}{}^{c,E}}{\rho}\right)^{\frac{1}{2}} \tag{105}$$

and

$$s_{44}{}^E=1/c_{44}{}^{c,E}. \tag{106}$$

An oriented cut is necessary to evaluate $s_{46}{}^E$. If we cut a crystal with the width and thickness both in the ZX plane and the length of the crystal along the Y axis, it can be shown that the shearing modulus $s_{66}'^E$ is equal to

$$s_{66}'^E=s_{66}{}^E\cos^2\theta-s_{46}{}^E\sin 2\theta+s_{44}{}^E\sin^2\theta. \tag{107}$$

At the same time $s_{26}'^E$ is equal to zero so that the resonant frequency of such a plate is determined by $c_{66}{}^{c,E\prime}$. The driving piezoelectric constant d_{14} is equal to

$$d_{14}'=d_{14}\cos^2\theta+\frac{(d_{16}-d_{34})}{2}\sin 2\theta-d_{36}\sin^2\theta. \tag{108}$$

Hence for a crystal cut with its thickness direction 45° from X, the elastic constant

$$\frac{1}{s_{66}{}^{E\prime}}=\frac{2}{(s_{66}{}^E-2s_{46}{}^E+s_{44}{}^E)}=c_{66}{}^{c,E\prime}. \tag{109}$$

The dielectric constants $\epsilon_{11}{}^T$, $\epsilon_{22}{}^T$, $\epsilon_{33}{}^T$ can be evaluated by measuring the capacities at low frequencies along the X, Y, and Z axes, respectively, while the dielectric constant $\epsilon_{13}{}^T$ can be evaluated by measuring the capacity of the above crystal which as shown involves the values

$$\frac{(\epsilon_{11}{}^T+2\epsilon_{13}{}^T+\epsilon_{33}{}^T)}{2}. \tag{110}$$

Hence all of the constants can be evaluated as explained above except the shear elastic constant s_{55}^E. This is more complicated since it involves measuring a coupled mode. For a Y cut crystal with its width or frequency determining direction along X, the shear coupling coefficient cannot be neglected and the shear resonant frequency is given by the equation

$$f=\frac{1}{2l_w}\left(\frac{(c_{11}{}^{c,E}+c_{55}{}^{c,E})-[(c_{11}{}^{c,E}-c_{55}{}^{c,E})^2+4c_{15}{}^{c,E^2}]^{\frac{1}{2}}}{2\rho}\right)^{\frac{1}{2}}$$

or

$$\frac{c_{11}{}^{c,E}+c_{55}{}^{c,E}-[(c_{11}{}^{c,E}-c_{55}{}^{c,E})^2+4(c_{15}{}^{c,E})^2]^{\frac{1}{2}}}{2}=(2l_wf)^2\rho. \qquad (111)$$

Finally we have from Eq. (55) transformed to the Y axis

$$c_{ij}{}^{c,E}=\frac{(-1)^{k+l}\Delta_{kl}}{\Delta}(k,\, l,\, =1,\, 2,\, 3), \qquad (112)$$

where Δ is the determinant

$$\Delta=\begin{vmatrix} s_{11}{}^E, & s_{13}{}^E, & s_{15}{}^E \\ s_{13}{}^E, & s_{33}{}^E, & s_{35}{}^E \\ s_{15}{}^E, & s_{35}{}^E, & s_{55}{}^E \end{vmatrix}.$$

Since all the $s_{ij}{}^E$ values have been determined but $s_{55}{}^E$, the two relations can be solved simultaneously for $s_{55}{}^E$ and all the elastic constants can be determined.

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Second Quantization and Representation Theory

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The formalism of the second quantization is developed entirely within the framework of the Dirac-Jordan representation theory. The equivalence of this formalism and the methods of ordinary coordinate-spin space is shown, and the equations of "connection" are fully developed. It is shown that the "creation" and "annihilation" operators, and indeed all operators which do not commute with the quantized Hamiltonian and hence whose representatives cannot be explicitly given in a configuration space of a fixed number of dimensions are easily treated in terms of the general representation theory and arise quite naturally. Both types of statistics are considered, and the Fock-Dirac density matrix and self-consistent field are treated as a simple illustration.

We consider the general properties of a system of n-indistinguishable particles, and compare the description of the system by two different operator sets x_r and $\mathbf{E}_r$ associated with the rth particle ($r=1,\, 2,\, \cdots n$). The operators $\mathbf{x}_r$ and $\mathbf{E}_r$ will in general stand for a complete commuting set of observables for each particle; thus for electrons for example we may take $\mathbf{x}_r=(\mathbf{x}_r,\, \mathbf{y}_r,\, \mathbf{z}_r,\, \boldsymbol{\sigma}_r)$; $\boldsymbol{\sigma}_r=\boldsymbol{\sigma}_{zr}$ and $\mathbf{E}_r=(\mathbf{H}_r,\, \mathbf{m}_r{}^2,\, \mathbf{m}_r,\, \boldsymbol{\sigma}_r)$; $\mathbf{m}_r=\mathbf{m}_{zr}$. However, for our general calculations we need only consider that the operators $\mathbf{E}_r$ have discrete spectra, without specifying their specific form beyond the condition that the operators (both $\mathbf{x}_r$ and $\mathbf{E}_r$) of any one particle commute with those of any other. All the $\mathbf{x}$'s together form a complete $\mathbf{x}$-representation and likewise the $\mathbf{E}$'s form an $\mathbf{E}$-representation.

Now any arbitrary physical state $|\,;t\rangle$ can be expanded in terms of the eigen-$|\rangle$ of either of these