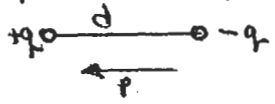
3.60 Symmetry, Structure and Tensor Properties of Materials

SOME BASIC RELATIONS IN ELECTROMAGNETISM

DIPOLE MOMENT : CONSIDER A PAIR OF POINT CHARGES OF EQUAL MAGNITUDE BUT OPPOSITE SIGN SEPARATED BY A DISTANCE d



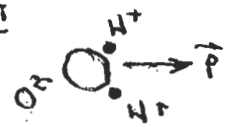
THE DIPOLE MOMENT IS DEFINED AS $|\vec{p}| = q \cdot \vec{d}$

IT IS ASSIGNED A VECTOR SENSE — PARALLEL TO $\vec{d}$ AND POINTING FROM THE NEGATIVE CHARGE TOWARD THE POSITIVE CHARGE

(IT IS A USEFUL DEFINITION BECAUSE THE VECTOR SENSE AND THE COMBINATION OF q AND d TOGETHER APPEAR IN CONSIDERATIONS SUCH AS THE ELECTRIC FIELD $\vec{\mathcal{E}}$ CREATED IN THE REGION AROUND THE DIPOLE OR IT COMPUTING THE TORQUE ON A DIPOLE WHEN IT IS PLACED IN AN ELECTRIC FIELD.)

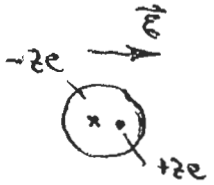
DIPOLES CAN BE EITHER

PERMANENT



OR INDUCED

(a) ATOM IN ELECTRIC FIELD



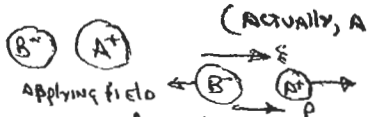
$$\vec{p} \propto \vec{\mathcal{E}}$$

$$\equiv \alpha \mathcal{E}$$

α → ELECTRONIC POLARIZABILITY

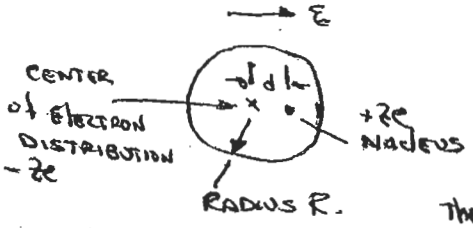
(ACTUALLY, A TENSOR! $P_i = \alpha_{ij} \mathcal{E}_j$)

OR INDUCED (b) — IONS IN A STRUCTURE



$P_i = \alpha_{ij} \mathcal{E}_j$ → IONIC POLARIZABILITY

LET'S CONSIDER A VERY SIMPLIFIED MODEL FOR THE DIELECTRIC POLARIZABILITY



WE REPRESENT THE ELECTRON CLOUD BY A SPHERE OF RADIUS R THAT HAS A UNIFORM CONCENTRATION OF ELECTRONS THROUGHOUT ITS VOLUME. ALSO, WE ASSUME THAT, WHEN THE ELECTRIC FIELD ACTS TO DISPLACE THE NUCLEUS AND THE ELECTRONS, THE SPHERICAL DISTRIBUTION DISTRIBUTION OF ELECTRONS IS NOT DEFORMED

THE CENTER OF THE ELECTRON DISTRIBUTION AND THE NUCLEUS WILL SEPARATE UNTIL THE FORCE ON THE CHARGES EXERTED BY THE ELECTRIC FIELD IS JUST BALANCED BY THE ATTRACTION BETWEEN NUCLEUS AND ELECTRONS.

THE DIPOLE MOMENT IS $Zed = p$

THE FORCE ON THE CHARGES EXERTED BY THE ELECTRIC FIELD $\mathcal{E}$ IS

$$F = Ze\vec{\mathcal{E}}$$ ($\vec{\mathcal{E}}$ IS FORCE PER UNIT + CHARGE)

DRAW A CIRCLE OF RADIUS d (THE SEPARATION OF THE CENTER OF THE ELECTRON DISTRIBUTION AND THE NUCLEUS) ABOUT THE CENTER OF THE ELECTRON SPHERE. THEN THE FORCE BETWEEN THE ELECTRONS AND NUCLEUS, IS (BY COULOMB'S LAW)

$$F = \frac{1}{4\pi\epsilon_0} \frac{Ze \cdot Q}{d^2}$$ WHERE Q IS THE CHARGE INSIDE THE SPHERE OF RADIUS d.

(WE USE THE FACT THAT A CHARGE PLACED WITHIN A UNIFORMLY-CHARGED SPHERE EXPERIENCES NO FORCE AT ANY POSITION

Q WILL BE $\frac{\frac{4}{3}\pi d^3}{\frac{4}{3}\pi R^3} \cdot Ze$

EQUATING THESE ELECTROSTATIC FORCES

$$ze\mathcal{E} = \frac{1}{4\pi\epsilon_0}\frac{ze\cdot Q}{d^2} = \frac{1}{4\pi\epsilon_0}\frac{ze}{d^2}\cdot\left(\frac{d^3}{R^3}\cdot ze\right)$$

SOLVING FOR d

$$d = \frac{4\pi\epsilon_0 R^3}{ze}\vec{\mathcal{E}}$$

AND THE DIPOLE MOMENT zed IS $\mu = \frac{4\pi\epsilon_0 R^3}{ze}\cdot ze\,\vec{\mathcal{E}}$

FROM WHICH $\boxed{\vec{P} = 4\pi\epsilon_0 R^3\,\vec{\mathcal{E}}}$

AND THE ELECTRONIC POLARIZABILITY IS

$$\boxed{\alpha = 4\pi\epsilon_0 R^3}$$

THIS VERY SIMPLIFIED MODEL IS INSTRUCTIVE AND AMUSING FOR TWO REASONS.

(1) IT PREDICTS THAT THE INDUCED DIPOLE MOMENT IS PREDICTED TO BE PROPORTIONAL TO $\vec{\mathcal{E}}$

(2) THE ELECTRONIC POLARIZABILITY IS SHOWN TO BE PROPORTIONAL TO THE VOLUME OF THE ATOM: BIG ATOMS ARE MUSHIER, WHICH IS IN FACT THE CASE. (Tl^+ HAS THE LARGEST IONIC POLARIZABILITY OF ANY CATION)

POLARIZABILITIES ARE RELATED TO INDEX OF REFRACTION, n, BY THE LORENZ-LORENTZ EQUATION

$$\frac{n^2-1}{n^2+2} = \frac{4\pi}{3}\sum N_i\alpha_i \quad \text{where } N_i \text{ is number of species } i \text{ per unit volume}$$

OR, IN ANOTHER FORM

$$M/\rho\,\frac{n^2-1}{n^2+2} = \frac{4\pi}{3}L\alpha \quad \text{where} \begin{cases} M = \text{MOLECULAR WEIGHT} \\ \rho = \text{DENSITY} \\ L = \text{AVOGADRO'S NUMBER} \\ \alpha = \text{POLARIZABILITY PER "MOLECULE"} \end{cases}$$

THE DIELECTRIC CONSTANT OF A MATERIAL, ϵ, IS RELATED TO INDEX OF REFRACTION BY

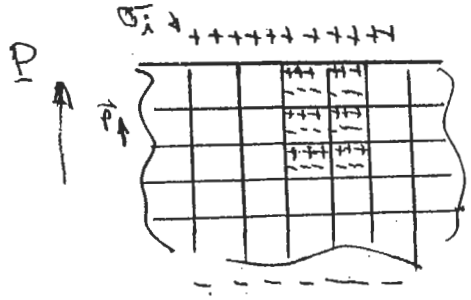
$$\epsilon = n^2$$

THE ABOVE RELATIONS MAY, THEREFORE, BE WRITTEN IN TERMS OF ϵ (UPON WHICH THEY BECOME KNOWN AS THE CLAUSIUS-MOSSOTTI EQUATIONS)

A SET OF ELECTRONIC POLARIZABILITIES FOR IONS HAVE BEEN DETERMINED ON THIS BASIS BY TESSMAN, KAHN AND SHOCKLEY (Phys. Rev. 92 890 (1953).)

MATTER IN BULK

THE DIPOLE MOMENT PER UNIT VOLUME IS DESIGNATED BY $\underline{P}$ AND HAS UNITS OF $\frac{\text{CHARGE} \cdot \text{LENGTH}}{\text{LENGTH}^3} = \frac{\text{CHARGE}}{\text{UNIT AREA}}$



LET EACH OF THE ATOMIC DIPOLES ABOVE BE REPRESENTED BY A CUBIC CELL OF EDGE δ WITH INDUCED CHARGES ON ITS SURFACE

THE DIPOLE MOMENT ON EACH ATOM IS

$$p = q_i \delta \quad \text{where } q_i \text{ IS THE INDUCED CHARGE}$$

THE NUMBER OF CELLS/UNIT VOLUME IS

$$n = \frac{\text{UNIT VOLUME}}{\text{VOL./CELL}} = \frac{1}{\delta^3}$$

SO THE DIPOLE MOMENT PER UNIT VOLUME, P IS

$$P = n p$$

$$= \frac{1}{\delta^3} \cdot q_i \delta$$

$$\boxed{P = \frac{q_i}{\delta^2}}$$ AN INDUCED CHARGE/UNIT AREA

WHILE THIS MODEL MAY SEEM OVERLY SIMPLE AND CRUDE THE DETAILS OF THE "CELLS" DO NOT MATTER BECAUSE CHARGE EVERYWHERE CANCELS INTERNALLY AND REMAINS UN-NEUTRALIZED ONLY ON THE SURFACE OF THE SPECIMEN

SO POLARIZATION, P, DIPOLE MOMENT/UNIT VOL. IS EQUALLY NUMERICALLY AND PHYSICALLY TO AN INDUCED CHARGE/UNIT AREA

Piezoelectricity

Piezoelectricity (literally "pressure electricity") is an important property that must be described in terms of a third-rank tensor. The property is the basis of a number of devices ranging from transducers, sensors and actuators through audio equipment down to everyday devices such as cigarette lighters

There are several distinct piezoelectric phenomena and we shall describe each in turn.

The Direct Piezoelectric Effect describes a dipole moment per unit volume (polarization, P) that is created when a material is subjected to an applied stress. The origin of the property can be quite simple in some materials. In an ionic material the creation of deformation through application of a stress moves charged ions relative to one another and thereby creates local dipole moments. (It is possible to calculate the magnitude of the property for simple structures if one knows the elastic properties)

We will follow the simple assumptions that we made for second-rank tensors — namely, we will assume a linear response and, second, that every component of the generalized displacement is given by a linear combination of each component of the generalized force. For the direct piezoelectric effect this means we write each component of the polarization vector as a linear combination of each of the nine components of the stress tensor

$$\boxed{P_i = d_{ijk}\sigma_{jk}}$$

P_i is a vector (tensor of first rank) and transforms according to the law for vectors

$$P_i' = c_{il}P_l \quad \text{where } c_{il} \text{ are the direction cosines for the change of axes.}$$

σ_{ij} is a tensor of second rank and transforms according to the law for 2nd rank tensors

$$\sigma_{ij}' = c_{il}c_{jm}\sigma_{lm}$$

From this it follows that d_{ijk} will transform according to

$$d_{ijk}' = c_{il}c_{jm}c_{kn}d_{lmn} \quad \text{and is, therefore, a tensor of third rank}$$

The elements d_{ijk} are called the piezoelectric moduli and are the coefficients in three equations for $P_1\ P_2\ P_3$ that involve all nine elements of stress

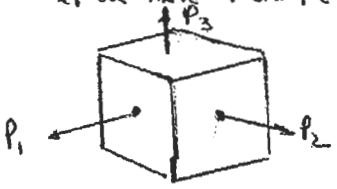
$$\begin{cases} P_1 = d_{111}\sigma_{11} + d_{122}\sigma_{22} + d_{133}\sigma_{33} + d_{123}\sigma_{23} + d_{132}\sigma_{32} + d_{113}\sigma_{13} + d_{131}\sigma_{31} + d_{112}\sigma_{12} + d_{121}\sigma_{21} \\ P_2 = d_{211}\sigma_{11} + \text{---} \\ P_3 = \text{---} \end{cases}$$

3 Eqs → 9 variables

$\therefore d_{ijk}$ is an array of $3 \times 9 = 27$ (!) elements

From the preceding lecture we saw that a consequence of polarization was an induced surface charge and that polarization (dipole moment/unit vol) is numerically equal to $\vec{P}$

If we have a sample in which a polarization has been induced in some general direction relative to surfaces normal to our reference axes $X_1\ X_2\ X_3$, the X_1 component of $\vec{P}$, P_1, will be equal to the charge per unit area on the surface normal to X_1, P_2 the charge per unit area on a surface normal to X_2 -- etc. Note that we can, through the geometry of the sample, create a specimen that emphasizes one charge density over another — for example a very thin plate in the X_1, X_2 plane will primarily



MEASURE P_3 — BIG SURFACE × CHARGE PER UNIT AREA = BIG CHARGE.

$\vec{P}$ MEASURES CHARGE/UNIT AREA $\left(\text{coulombs}/m^2\right)$ AND σ_{ij} IS FORCE/UNIT AREA $\left(\text{NEWTONS}/m^2\right)$

THEREFORE: $P\left(\text{coulombs}/m^2\right) = d\,\sigma\left(\text{NEWTONS}/m^2\right)$ THE UNITS of d_{ijk} ARE $\frac{\text{Coulombs}}{\text{NEWTON}}$

CHARGE PER UNIT FORCE.

If the CHARGE INDUCED ON A SURFACE IS POSITIVE THEN P_i IS POSITIVE (RECALL THAT, ON AN ATOMIC SCALE DIPOLE MOMENT IS A VECTOR DIRECTED FROM THE ⊖ CHARGE TO THE ⊕ CHARGE ALONG THE VECTOR SEPARATING THE CHARGES) If the INDUCED DIPOLE MOMENT IS ONE THAT CREATES ⊕ CHARGE ON A SURFACE THAT, MACROSCOPICALLY, A POSITIVE $\vec{P}$ IS ONE THAT IS PARALLEL TO THE INDUCED DIPOLE MOMENTS.

NOTE THAT THE NATURE of the RELATION $P_i = d_{ijk}\,\sigma_{jk}$ SAYS THAT if P IS, SAY, ⊕ FOR A GIVEN STATE of STRESS (ie POSITIVE CHARGE ON THE SURFACE OUT of which $\vec{P}$ IS DIRECTED) THEN REVERSING THE SIGN of σ (eg, GOING FROM TENSILE TO COMPRESSIVE) CHANGES THE SIGN of THE INDUCED SURFACE CHARGE AND THE DIRECTION of $\vec{P}$.

CONVERSION TO MATRIX NOTATION

LET US EXAMINE ONE LINE of THE TENSOR RELATION BETWEEN P_i AND σ_{jk}. FOR EXAMPLE

$$P_1 = d_{1(11)}\sigma_{(11)} + d_{1(22)}\sigma_{(22)} + d_{1(33)}\sigma_{(33)} + d_{1(23)}\sigma_{(23)} + d_{1(32)}\sigma_{(32)} + d_{1(31)}\sigma_{(31)} + d_{1(13)}\sigma_{(13)} + d_{112}\sigma_{12} + d_{121}\sigma_{21}$$

A FEATURE of this RELATION IS THAT THE SECOND TWO SUBSCRIPTS ON d_{ijk} ALWAYS ACT IN PAIRS THIS RAISES A QUESTION of WHETHER WE SHOULD KEEP THIS AWKWARD TENSOR NOTATION.

(THE NOTATION, IN FACT, GROWS INCREASINGLY CUMBERSOME AS THE RANK of THE TENSOR INCREASES!) WHY DON'T WE SIMPLIFY LIFE BY USING A SINGLE SYMBOL TO REPRESENT THE RELATION BETWEEN POLARIZATION AND STRESS?

TO ANSWER THAT QUESTION — if WE MOVE TO A TWO-SUBSCRIPT NOTATION WE HAVE LOST THE INDICES ON THE TENSOR ELEMENTS AND NO LONGER HAVE THE INFORMATION NEEDED TO TRANSFORM FROM ONE COORDINATE SYSTEM TO ANOTHER. IN SHORT, WE WILL HAVE A MATRIX RELATION AND NOT A TENSOR EXPRESSION. THIS IS of SMALL CONCERN TO A DEVICE ENGINEER WHOSE WORK INVOLVES, SAY, WORKING WITH QUARTZ WAFERS THAT ARE CUT IN A PARTICULAR, NEVER-CHANGING CRYSTALLOGRAPHIC ORIENTATION. If THE NEED ARISES TO REFER THE PROPERTIES TO A DIFFERENT COORDINATE SYSTEM, HOWEVER, WE MUST BE CONSTANTLY PREPARED TO RESURRECT THE FULL THREE SUBSCRIPT TENSOR NOTATION.

THE NUMBERS THAT DESCRIBE PIEZOELECTRIC BEHAVIOR ARE, HOWEVER, INVARIABLY REPORTED IN MATRIX FORM REFERRED TO REFERENCES AXES WHOSE RELATION TO CRYSTALLOGRAPHIC AXES AND SYMMETRY ELEMENTS IS ESTABLISHED BY NOMENCLATURE COMMITTEES of RELEVANT PROFESSIONAL SOCIETIES.

THE CONVENTION FOR SWITCHING THE LAST TWO INDICES TO A SINGLE SYMBOL EASY TO REMEMBER FROM THE FOLLOWING: TAKE A PATH THROUGH THE STRESS TENSOR AS follows:

WITH THIS CONVENTION WE CAN BEGIN TO WRITE

TENSOR: $P_1 = d_{111}\sigma_{11} + d_{122}\sigma_{22} + d_{133}\sigma_{33} +$ } whoops! NOW WE HAVE A PROBLEM!!

MATRIX $P_1 = d_{11}\sigma_1 + d_{12}\sigma_2 +$

WHEN WE ENCOUNTER THE OFF-DIAGONAL ELEMENTS of SHEAR STRESS WE HAVE TWO ELEMENTS THAT CARRY THE SAME TWO SUBSCRIPTS. MOREOVER, WHEN $i \neq j$ $\sigma_{ij} = \sigma_{ji}$ AND YOU CANNOT HAVE ONE WITHOUT THE OTHER if THE BODY IS IN MECHANICAL EQUILIBRIUM.

THEREFORE, ATTEMPTING TO CONTINUE

TENSOR: $P_1 = \sim + d_{123}\sigma_{23} + d_{132}\sigma_{32} + d_{131}\sigma_{31} + d_{113}\sigma_{13} + d_{112}\sigma_{12} + d_{121}\sigma_{21}$

MATRIX: $d_{14}\sigma_4 + d_{14}\sigma_4 + d_{15}\sigma_5 + d_{15}\sigma_5 + d_{16}\sigma_6 + d_{16}\sigma_6$

This is TERRIBLE!! WE CAN'T APPLY A σ_{23} WITHOUT AN EQUAL σ_{32} — SO, how ARE WE TO MEASURE d_{123} AND d_{132} INDEPENDENTLY? ARE THEY EQUAL ($d_{123} = d_{132}$)? How CAN WE TELL? ARE WE GOING TO HAVE TO MODIFY OUR NOTATION SUCH THAT WE CAN KEEP d_{132} AND d_{123} DISTINGUISHABLE? If SO, WE ARE BACK TO A 3 x 9 ARRAY of ELEMENTS AND THERE IS NO POINT OR GAIN IN GOING from TENSOR TO MATRIX NOTATION. If WE CAN'T MEASURE d_{132} AND d_{123} SEPARATELY, SHALL WE ASSUME THAT THEY ARE EQUAL? WHY NOT, if WE CAN ONLY EXPERIMENTALLY MEASURE THEIR COMBINATION??

BUT THEN DO WE WRITE

$$d_{123}\sigma_{23} + d_{132}\sigma_{32} \longrightarrow d_{14}\sigma_4 + d_{14}\sigma_4 = 2d_{14}\sigma_4 \; ??$$

IN OTHER WORDS DO WE SAY $P_i = d_{ij}\sigma_j$ for $j = 1,2,3$

BUT $P_i = 2d_{ij}\sigma_j$ for $j = 4,5,6$ FINE MATRIX THAT WOULD BE!!

THERE IS EFFICIENCY IN A MATRIX RELATION HOWEVER, AND IT IS SENSIBLE TO WRITE

$$P_i = d_{ij}\sigma_j \quad \text{for } i = 1,2,3 \text{ AND } j = 1,2,3 \text{ PLUS } 4,5 \& 6$$

THE ONLY WAY TO DO THIS IS TO ABSORB THE FACTOR of 2 IN DEFINING THE MATRIX PIEZOELECTRIC MODULI AND SAY $d_{ijk} \equiv d_{ij}$ if $j = k = 1,2$ OR 3

BUT $d_{ijk} + d_{ikj} \equiv d_{ij}$ if $j = 4,5,$ OR 6

(This PROBLEM of HIDING A FACTOR 2 GETS PROGRESSIVELY WORSE with higher-RANK TENSORS!)

BY GOING TO MATRIX NOTATION WE HAVE GONE from $3 \times 9 = 27$ TENSOR ELEMENTS TO $3 \times 6 = 18$ MATRIX ELEMENTS

THE CONVERSE PIEZOELECTRIC EFFECT

This is, SEEMINGLY, A DIFFERENT TYPE of 3RD RANK TENSOR PROPERTY. IT DESCRIBES THE FACT THAT if ONE APPLIES AN ELECTRIC FIELD TO A CRYSTAL A STATE of STRAIN IS INDUCED. This is PERHAPS NOT SURPRISING: IN AN IONIC CRYSTAL AN ELECTRIC FIELD WOULD PULL POSITIVE IONS IN ONE DIRECTIONS AND ANIONS IN THE OPPOSITE DIRECTION AND This is SURELY NOT UNEXPECTED.

WE COULD WRITE THEREFORE $\epsilon_{jk} = T_{jki}\mathcal{E}_i$ which WOULD BE A SET of NINE EQUATIONS → IN THREE VARIABLES, THE COMPONENTS of $\mathcal{E}$

9 ↓ THUS A $9 \times 3 = 27$ ELEMENTS IN THE ARRAY

(STILL A THIRD RANK TENSOR — THREE SUBSCRIPTS — AND STILL THE SAME LAW of TRANSFORMATION)

WHAT IS SURPRISING — VERY SURPRISING, IN FACT, IS THAT THE SAME ARRAY of COEFFICIENTS SERVE TO DESCRIBE BOTH THE DIRECT AND THE CONVERSE PIEZOELECTRIC EFFECTS!!

TO BE ABLE TO WRITE THE CONVERSE PIEZOELECTRIC EFFECT IN TERMS OF THE PIEZOELECTRIC MODULI, HOWEVER, ONE MUST BEND THE CONVENTIONS FOR SUMMATIONS OVER REPEATED SUBSCRIPTS A LITTLE BIT AND WRITE $\epsilon_{(jk)} = d_{i(jk)} \mathcal{E}_{(i)}$ (NOTE THE REVERSED ORDER of the SUBSCRIPTS!) THIS RELATION COMES FROM A THERMODYNAMIC ARGUMENT AND NOT FROM TENSOR FORMALISM

THERE IS ONE INTERESTING CONSEQUENCE OF THE CONVERSE PIEZOELECTRIC EFFECT THAT HAS BEARING ON THE AMBIGUITIES THAT WE ENCOUNTERED IN GOING FROM TENSOR TO MATRIX NOTATION IN THE CASE OF THE DIRECT PIEZOELECTRIC EFFECT. WRITING OUT A FEW LINES OF THE EQUATIONS

$$\epsilon_{11} = d_{111}\mathcal{E}_1 + d_{211}\mathcal{E}_2 + d_{311}\mathcal{E}_3$$
$$\epsilon_{22} = d_{122}\mathcal{E}_1 + d_{222}\mathcal{E}_2 + d_{322}\mathcal{E}_3$$
$$\epsilon_{33} = d_{133}\mathcal{E}_1 + d_{233}\mathcal{E}_2 + d_{333}\mathcal{E}_3$$
$$\vdots$$
$$\epsilon_{23} = d_{123}\mathcal{E}_1 + d_{223}\mathcal{E}_2 + d_{323}\mathcal{E}_3$$
$$\epsilon_{32} = d_{132}\mathcal{E}_1 + d_{232}\mathcal{E}_2 + d_{332}\mathcal{E}_3$$

THESE THREE EQUATIONS GIVE AN ANSWER TO A QUESTION THAT WE HAVE NOT YET ASKED: CAN APPLICATION OF AN ELECTRIC FIELD CAUSE A VOLUME CHANGE? $\epsilon_{11}+\epsilon_{22}+\epsilon_{33}$ = TRACE of the STRAIN TENSOR $= \frac{\Delta V}{V}$ IF THE TERMS ON THE RIGHT ARE ZERO FOR ANY $\mathcal{E}_i$ THERE CAN BE NO VOLUME CHANGE!!

BUT $\epsilon_{23} \equiv \epsilon_{32}$ BY DEFINITION of the STRAIN TENSOR!

IF WE WERE TO APPLY AN ELECTRIC FIELD WITH ONLY AN $\mathcal{E}_1$ COMPONENT

$$\epsilon_{23} = d_{123}\mathcal{E}_1$$
$$\epsilon_{32} = d_{132}\mathcal{E}_1$$

BUT $\epsilon_{23} \equiv \epsilon_{32}$ $\therefore d_{123} \equiv d_{132}$ THEREFORE, ALTHOUGH WE COULD NOT MEASURE d_{ijk} AND d_{ikj} INDIVIDUALLY ON THE BASIS of the DIRECT PIEZOELECTRIC EFFECT WE CAN DO SO IN THE CONVERSE PIEZOELECTRIC EFFECT. THUS $\boxed{d_{ijk} \equiv d_{ikj}}$

UNFORTUNATELY, THE NASTY FACTOR of 2 THAT WE ENCOUNTERED IN THE DIRECT PIEZOELECTRIC EFFECT NOW REAPPEARS TO CAUSE TROUBLE AGAIN. WE HAD WRITTEN

$P_i = d_{ij}\sigma_j$ IN MATRIX FORM. IN ORDER TO DO SO WE HAD TO ABSORB A FACTOR of TWO WHEN WE WROTE, FOR EXAMPLE,

$$P_1 = \cdots + d_{123}\sigma_{23} + d_{132}\sigma_{32} + d_{131}\sigma_{31} + d_{113}\sigma_{13} + d_{121}\sigma_{21} + d_{112}\sigma_{12}$$
$$= \cdots + d_{123}\sigma_4 + d_{132}\sigma_4 + d_{131}\sigma_5 + d_{113}\sigma_5 + d_{121}\sigma_6 + d_{112}\sigma_6$$
$$= \cdots + (d_{123}+d_{132})\sigma_4 + (d_{131}+d_{113})\sigma_5 + (d_{121}+d_{112})\sigma_6$$

WE OBSERVED THAT WE COULD NOT APPLY A σ_{32} WITHOUT APPLYING AN IDENTICAL σ_{23} AND SO IT SEEMED THAT WE COULDN'T MEASURE d_{123} AND d_{132} INDIVIDUALLY. IT THEREFORE SEEMED REASONABLE TO LUMP THEM TOGETHER INTO A SINGLE MATRIX ELEMENT.

WE NOW KNOW THAT $d_{123} \equiv d_{132}$ AS A RESULT of THE CONVERSE PIEZOELECTRIC EFFECT! WE CAN THEREFORE WRITE

$$P_1 = \cdots + 2d_{123}\sigma_4 + 2d_{113}\sigma_5 + 2d_{112}\sigma_6$$

AND THEN DEFINED $\quad d_{14}\sigma_4 + d_{15}\sigma_5 + d_{16}\sigma_6$

THEREFORE
$$\begin{cases} d_{123} = d_{132} = \frac{1}{2}d_{14} \\ d_{113} = d_{131} = \frac{1}{2}d_{15} \\ d_{112} = d_{121} = \frac{1}{2}d_{16} \end{cases}$$

NOW WE ENCOUNTER TROUBLE! IF WE NOW ATTEMPT TO WRITE THE CONVERSE EFFECT IN MATRIX FORM
$$\epsilon_{23} = d_{123}\mathcal{E}_1 + d_{223}\mathcal{E}_2 + d_{323}\mathcal{E}_3$$
$$\epsilon_{32} = \tfrac{1}{2}d_{14}\mathcal{E}_1 + \tfrac{1}{2}d_{24}\mathcal{E}_2 + \tfrac{1}{2}d_{34}\mathcal{E}_3$$

AND NOW WE CANNOT WRITE A MATRIX RELATION WITHOUT SOME TERMS HAVING A FACTOR ½ AND SOME NOT! WE MUST HIDE THE FACTOR 2 SOMEPLACE ELSE AND THE ONLY PLACE LEFT IS IN THE DEFINITION of MATRIX STRAIN

WE ARE THUS FORCED TO WRITE

$$\begin{bmatrix} \epsilon_{11} & \epsilon_{12} & \epsilon_{13} \\ \epsilon_{21} & \epsilon_{22} & \epsilon_{23} \\ \epsilon_{31} & \epsilon_{32} & \epsilon_{33} \end{bmatrix} \longrightarrow \begin{bmatrix} \epsilon_1 & \frac{1}{2}\epsilon_6 & \frac{1}{2}\epsilon_5 \\ \frac{1}{2}\epsilon_6 & \epsilon_2 & \frac{1}{2}\epsilon_4 \\ \frac{1}{2}\epsilon_5 & \frac{1}{2}\epsilon_4 & \epsilon_3 \end{bmatrix}$$

SYMMETRY RESTRICTIONS ON PIEZOELECTRIC MODULI (d_{ij})

WE HAVE BECOME FAMILIAR WITH THE PROCEDURE FOR DERIVING THESE CONSTRAINTS IN CONSIDERING SECOND RANK TENSORS. THE PROCESS IS EXACTLY ANALAGOUS FOR THIRD-RANK TENSORS EXCEPT THAT WE MUST, FIRST, CONVERT FROM MATRIX FORM TO TENSOR FORM IN ORDER TO HAVE All THREE PROPER SUBSCRIPTS FOR d_{ij} AND, SECOND, THERE ARE MORE DIRECTION COSINES IN THE SUMMATION FOR THE TRANSFORMED ELEMENT ($d'_{ijk} = C_{il}C_{jm}C_{kn}d_{lmn}$) AND THERE ARE A GREAT MANY ELEMENTS TO BE TRANSFORMED AND A GREAT MANY MORE TERMS IN EACH SUMMATION.

LET'S PERFORM A TRANSFORMATION FOR TWO ELEMENTS JUST TO REMIND OURSELVES HOW IT WORKS

(a) d_{13} IN A MONOCLINIC CRYSTAL WITH SYMMETRY 2 (ORIENTED ALONG X_3)

$d_{13} \equiv d_{133}$ USING THE METHOD OF DIRECT INSPECTION $X_1 X_2 X_3 \longrightarrow -X_1 - X_2 + X_3$

d_{ijk}	$X_i X_j X_k$	$X'_i X'_j X'_k$	d'_{ijk}
d_{133}	$X_1 X_3 X_3$	$X'_1 X'_3 X'_3 = -X_1 X_3 X_3$	$-d_{133} = +d_{133} = 0$

IF TENSOR IS TO STAY INVARIENT

$\therefore d_{133} = 0$

(b) d_{13} IN A MONOCLINIC CRYSTAL WITH SYMMETRY m (ORIENTED $\perp X_3$)

$d_{13} \equiv d_{133}$ TRANSFORMATION OF AXES IS $X_1 X_2 X_3 \longrightarrow X_1 X_2 - X_3$

d_{ijk}	$X_i X_j X_k$	$X'_i X'_j X'_k$	d'_{ijk}
d_{133}	$X_1 X_3 X_3$	$X'_1 X'_3 X'_3 = X_1 - X_3 - X_3$	$d_{133} \equiv d_{133}$ NO CONSTRAINT

NOTICE THAT CRYSTALS of SYMMETRY 2 AND m ARE BOTH MONOCLINIC AND YET THE CONSTRAINTS ON d_{133} ARE QUITE DIFFERENT (UNLIKE EVEN-RANK TENSORS FOR WHICH All MONOCLINIC CRYSTALS MUST DISPLAY THE SAME CONSTRAINTS

SYMMETRY RESTRICTIONS ON PIEZOELECTRIC MODULI (d_{ij})

CENTROSYMMETRIC SYMMETRY : All $d_{ij} \equiv 0$

($\bar{1}$, $2/m$, $\frac{2}{m}\frac{2}{m}\frac{2}{m}$, $4/m$, $\frac{4}{m}\frac{2}{m}\frac{2}{m}$, $\bar{3}$, $\bar{3}2/m$, $6/m$, $\frac{6}{m}\frac{2}{m}\frac{2}{m}$, $\frac{2}{m}\bar{3}$, $\frac{4}{m}\bar{3}\frac{2}{m}$)

TRICLINIC (1)

$$\begin{matrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{matrix} \quad (18)$$

MONOCLINIC 2 ($\parallel X_3$)

$$\begin{matrix} 0 & 0 & 0 & d_{14} & d_{15} & 0 \\ 0 & 0 & 0 & d_{24} & d_{25} & 0 \\ d_{31} & d_{32} & d_{33} & 0 & 0 & d_{36} \end{matrix} \quad (8)$$

MONOCLINIC m ($\perp X_3$)

$$\begin{matrix} d_{11} & d_{12} & d_{13} & 0 & 0 & d_{16} \\ d_{21} & d_{22} & d_{23} & 0 & 0 & d_{26} \\ 0 & 0 & 0 & d_{34} & d_{35} & 0 \end{matrix} \quad (10)$$

ORTHORHOMBIC

222 ($\parallel X_1, X_2, X_3$)

$$\begin{matrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & d_{25} & 0 \\ 0 & 0 & 0 & 0 & 0 & d_{36} \end{matrix}$$ (3)

2MM ($2 \parallel X_3$)

$$\begin{matrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{24} & 0 & 0 \\ d_{31} & d_{32} & d_{33} & 0 & 0 & 0 \end{matrix}$$ (5)

TETRAGONAL

4 ($\parallel X_3$)

$$\begin{matrix} 0 & 0 & 0 & d_{14} & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & -d_{14} & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{matrix}$$ (4)

$\bar{4}$

$$\begin{matrix} 0 & 0 & 0 & d_{14} & d_{15} & 0 \\ 0 & 0 & 0 & -d_{15} & d_{14} & 0 \\ d_{31} & -d_{31} & 0 & 0 & 0 & d_{16} \end{matrix}$$ (4)

422 ($4 \parallel X_3$)

$$\begin{matrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & -d_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{matrix}$$ (1)

4MM ($4 \parallel X_3$)

$$\begin{matrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{matrix}$$ (3)

$\bar{4}$2M ($\bar{4} \parallel X_3$, $2 \parallel X_1$)

$$\begin{matrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & d_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & d_{36} \end{matrix}$$ (2)

CUBIC

432

$$\begin{matrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{matrix}$$ (0)

ALL MODULI ARE ZERO!

$\bar{4}$3M AND 23

$$\begin{matrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & d_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & d_{14} \end{matrix}$$ (1)

HEXAGONAL

3 ($\parallel X_3$)

$$\begin{matrix} d_{11} & -d_{11} & 0 & d_{14} & d_{15} & +2d_{21} \\ d_{21} & -d_{21} & 0 & d_{15} & -d_{14} & -2d_{11} \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{matrix} \quad (6)$$

32 ($3 \parallel X_3$, $2 \parallel X_1$)

$$\begin{matrix} d_{11} & -d_{11} & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & -d_{14} & -2d_{11} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{matrix} \quad (2)$$

3m ($3 \parallel X_3$, $m \perp X_1$)

$$\begin{matrix} 0 & 0 & 0 & 0 & d_{15} & 2d_{21} \\ d_{21} & -d_{21} & 0 & d_{15} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{matrix} \quad (4)$$

6 $\quad$ (4)

$$\begin{matrix} 0 & 0 & 0 & d_{14} & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & -d_{14} & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{matrix}$$

SAME AS FOR **4**

6mm

$$\begin{matrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{matrix} \quad (3)$$

SAME RESULT AS FOR **4mm**

622

$$\begin{matrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & -d_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{matrix} \quad (1)$$

SAME ~~RESULT~~ AS FOR **422**

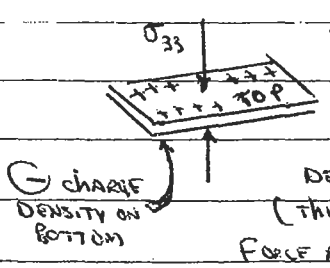
$\bar{6} = \frac{3}{m}$

$$\begin{matrix} d_{11} & -d_{11} & 0 & 0 & 0 & 2d_{21} \\ d_{21} & -d_{21} & 0 & 0 & 0 & -2d_{11} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{matrix} \quad (2)$$

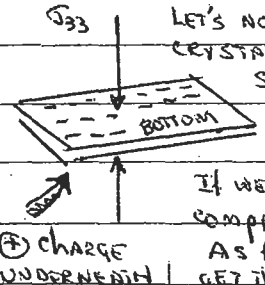
$\bar{6}m2$ ($m \perp X_1$)

$$\begin{matrix} 0 & 0 & 0 & 0 & 0 & 2d_{21} \\ d_{21} & -d_{21} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{matrix} \quad (1)$$

THE REASON FOR SOME OF THE ABOVE CONSTRAINTS CAN BE UNDERSTOOD FROM A SIMPLE PHYSICAL ARGUMENT. FOR EXAMPLE, IF A CRYSTAL POSSESSES INVERSION SYMMETRY IT CANNOT BE PIEZOELECTRIC ($All\ d_{ij} \equiv 0$)



SUPPOSE WE HAVE A PLATE SHAPED CRYSTAL AND SQUEEZE IT WITH A COMPRESSIVE STRESS σ_{33}. SUPPOSE THE SURFACE DEVELOPS A POSITIVE CHARGE DENSITY (THIS MEANS $\vec{P}_3$ IS ANTI-PARALLEL TO THE FORCE ALONG X_3)



LET'S NOW INVERT THE CRYSTAL. THE BOTTOM SURFACE (AND THE ⊖ CHARGE!) IS NOW ON TOP

IF WE APPLY THE SAME ~~COMPRESSIVE STRESS~~ AS BEFORE WE SHOULD GET THE SAME RESULT AS BEFORE IF THE CRYSTAL IS LEFT UNCHANGED BY INVERSION. BUT THE POLARITY OF THE CHARGE IS CHANGED AND HAS NOT REMAINED INVARIENT. THE RESULT IS IMPOSSIBLE.

OTHER PIEZOELECTRIC EFFECTS

THERE ARE TWO OTHER PIEZOELECTRIC EFFECTS THAT WE CAN MENTION. THEY ARE NOT DIGNIFIED WITH SPECIAL NAMES OF A SPECIFIC "EFFECT".

IF WE APPLY A STRESS TO INDUCE A POLARIZATION (THE "DIRECT PIEZOELECTRIC EFFECT") WE WILL ALSO INDUCE A STRAIN AS A CONSEQUENCE OF THAT STRESS. THEREFORE, WE COULD WRITE A RELATION BETWEEN INDUCED POLARIZATION AND STRAIN

$$P_i = e_{ijk}\,\epsilon_{jk}$$

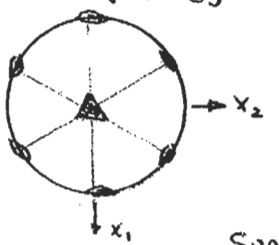
SIMILARLY, IN THE CONVERSE PIEZOELECTRIC EFFECT, IF AN ELECTRIC FIELD INDUCES A STATE OF STRAIN, THE MATERIAL MUST ALSO BE UNDER STRESS AND

$$\sigma_{jk} = -e_{ijk}\,\mathcal{E}_i$$

NOTE, AGAIN THE TRANSPOSED ORDER OF SUBSCRIPTS RELATIVE TO CONVENTION IN TENSOR NOTATION. THE RELATIONSHIP BETWEEN e_{ijk} AND $-e_{ijk}$ AGAIN follows from thermodynamic principles and NOT from symmetry requirements.

EXAMPLES OF PIEZOELECTRIC MATERIALS

(1) QUARTZ (SiO_2) POINT GROUP 32



THE "STANDARD" REFERENCE AXES ARE AS SHOWN. THE MATRIX OF PIEZOELECTRIC MODULI IS

$$d_{ij} = \begin{bmatrix} -2.3 & 2.3 & 0 & -0.67 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0.67 & 4.6 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \times 10^{-12} \text{ coul/newton}$$

QUARTZ IS NOT AN ESPECIALLY STRONG PIEZOELECTRIC MATERIAL.

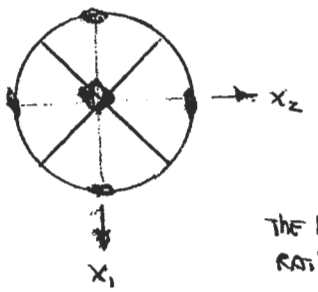
SUPPOSE WE APPLY A FIELD OF 100 VOLTS/CM $= 10^4$ V/m ALONG THE 2-FOLD AXIS DIRECTED ALONG x_1. THEN, FROM THE CONVERSE PIEZOELECTRIC EFFECT

$$\epsilon_1 = d_{11}\mathcal{E}_1 = -2.3\,10^{-12} \cdot 10^4 = -2.3\,10^{-8}$$

NOT A VERY LARGE STRAIN!

WHAT MAKES QUARTZ USEFUL AS A PIEZOELECTRIC MATERIAL IS ITS LOW COST, CHEMICAL STABILITY, AND VERY GOOD MECHANICAL PROPERTY. A MATERIAL THAT WILL EARN ITS LIVING BEING SQUEEZED CANNOT BE SOFT AND EASILY DEFORMED!

(2) AMMONIUM DIHYDROGEN PHOSPHATE (ADP) POINT GROUP $\bar{4}2m$



$$d_{ij} = \begin{bmatrix} 0 & 0 & 0 & 1.7 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1.7 & 0 \\ 0 & 0 & 0 & 0 & 0 & 51.7 \end{bmatrix} 10^{-12} \text{ coul/newton}$$

NOTE THE VERY LARGE VALUE OF d_{33} – MORE THAN 10 TIMES THE LARGEST MODULUS IN QUARTZ. THE MATERIAL, UNFORTUNATELY, IS RATHER SOFT AND IS ATTACKED BY MOISTURE.

THERE IS AN EXCITING NEW FAMILY OF PIEZOELECTRIC MATERIALS THAT HAS BEEN DISCOVERED VERY RECENTLY. THEY ARE PEROVSKITE-RELATED CERAMICS THAT HAVE PIEZOELECTRIC MODULI OVER AN ORDER OF MAGNITUDE LARGER THAN ANYTHING PREVIOUSLY KNOWN. $0.955\,Pb(Zn_{1/3}Nb_{2/3})O_3 - 0.45\,PbTiO_3$ HAS $d_{33} > 2000$ PC/NEWTON.* [FOR LITERATURE SEE J. YIN, B. JIANG AND W. CAO, IEEE TRANS. ON ULTRASONICS, FERROELECTRICS AND FREQUENCY CONTROL 47 [1] JAN 2000, 285-291.]

SOME OF THESE MATERIALS HAVE SHOWN STRAINS UP TO 0.85 %!!!

*($\rho = P/CO = 10^{-12}$) STATED ANOTHER WAY, 2000 10^{-12} COULOMB/NEWTON IS $10^3 \times d_{11}$ FOR QUARTZ!

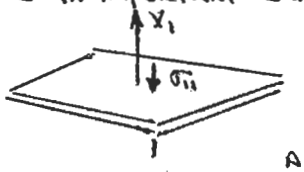
REPRESENTATION SURFACES.

UNFORTUNATELY, IT IS NOT POSSIBLE TO CREATE ANY REPRESENTATION SURFACE (SUCH AS THE REPRESENTATION QUADRIC FOR SECOND-RANK TENSORS) THAT GIVES A VIEW OF HOW HIGHER-RANK TENSOR PROPERTIES. CONSIDER THE CONVERSE PIEZOELECTRIC EFFECT. WE APPLY AN ELECTRIC FIELD IN A GIVEN DIRECTION (THAT PART IS EASY! WE HANDLED THAT QUESTION FOR SECOND RANK TENSOR PROPERTIES!) BUT THEN WHAT RESULTS IS A STRAIN - A TENSOR! HOW DO WE REPRESENT THAT AS A FUNCTION OF THE DIRECTION OF $\vec{\mathcal{E}}$? THERE ARE SIX INDEPENDENT ELEMENTS OF STRAIN!! SHOULD WE TRY TO VISUALIZE SIMULTANEOUSLY SIX DIFFERENT REPRESENTATION QUADRICS ?? THIS IS HARDLY USEFUL!

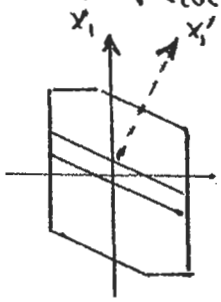
WHAT WE CAN DO, HOWEVER, IS TO APPLY A VECTOR OR SOMETHING LIKE A UNIAXIAL STRESS THAT IS SPECIALIZED BUT FOR WHICH "DIRECTION" IS UNAMBIGUOUSLY SPECIFIED. WE THEN EXAMINE — PERHAPS THROUGH A SAMPLE OF SPECIALIZED GEOMETRY SUCH AS A ROD OR PLATE — ONE OF THE COMPONENTS OF THE GENERALIZED DISPLACEMENT WE CAN THEN ASK HOW THIS COMPONENT OF DISPLACEMENT VARIES WITH THE DIRECTION OF THE GENERALIZED FORCE OR SOME COMPONENT THEREOF.

THE LONGITUDINAL PIEZOELECTRIC EFFECT

THIS IS AN IMPORTANT SCALAR MODULUS. WE CUT A VERY THIN PLATE OF THE MATERIAL. DEFINE ITS NORMAL AS THE DIRECTION OF X_1. WE THEN APPLY A UNIAXIAL STRESS σ_1 ALONG X_1. THIS WILL, IN GENERAL CREATE A POLARIZATION $\vec{P}$ IN A GENERAL ORIENTATION. SURFACE CHARGE DENSITY WILL THUS BE INDUCED ON ALL SURFACES OF THE PLATE BUT, AS THE SURFACE NORMAL TO X_1 IS MUCH LARGER IN AREA THAN THE VERY THIN AREAS PARALLEL TO X_1, MOST OF THE TOTAL CHARGE ON THE PLATE WILL BE DUE TO THE CHARGE DENSITY ON THE LARGE SURFACE NORMAL TO X_1. THE GEOMETRY OF THE PLATE, THEREFORE, MEANS THAT UPON APPLYING A COMPRESSIVE STRESS σ_1 WE MEASURE THE POLARIZATION COMPONENT P_1. THE QUANTITY RELATING THE TWO VARIABLES IS DEFINED AS THE LONGITUDINAL PIEZOELECTRIC MODULUS AND IT IS OBVIOUSLY THE SAME QUANTITY AS THE PIEZOELECTRIC MODULUS d_{11}



$$P_1 = d\,\sigma_1 = d_{11}\,\sigma_1$$



WE CAN NOW ASK THE FOLLOWING QUESTION: IF I WERE TO CUT A SIMILAR PLATE FROM THE CRYSTAL WITH ITS NORMAL IN A DIFFERENT DIRECTION, ALONG X_1', SAY, HOW WILL THE LONGITUDINAL PIEZOELECTRIC MODULUS CHANGE? WE WOULD APPLY A SIMILAR COMPRESSIVE STRESS ALONG X_1' SO THIS WOULD BE σ_1' AND MEASURE THE COMPONENT P_1' ALONG X_1'

THE EXPERIMENT WOULD BE

$$P_1' = d_{11}' \sigma_1' \qquad \text{WE ARE ASKING, THEREFORE, FOR THE VALUE OF } d_{11}'$$

AS A FUNCTION OF THE ORIENTATION OF X_1', THE NORMAL TO THE PLATE.

THE WAY ONE SOLVES THIS PROBLEM IS THE SAME FOR ALL SCALAR MODULI THAT REPRESENT BEHAVIOR OF HIGHER-RANK TENSOR PROPERTIES:

(1) CONVERT THE MATRIX ELEMENTS TO PROPER TENSOR SUBSCRIPTS AND REMOVE FACTORS OF 2
(2) REPLACE THE SUBSCRIPTS ON ANY ELEMENT THAT WE HAVE WRITTEN INCORRECTLY TO EMPHASIZE AN EQUALITY
(3) PERFORM THE TRANSFORMATION OF THE TENSOR ELEMENT USING $a'_{ijk\ldots} = c_{iq}c_{jm}c_{kn}\ldots a_{qmn\ldots}$
(4) RESTORE THE EQUALITIES BETWEEN ELEMENTS
(5) COLLAPSE THE SUBSCRIPTS BACK TO MATRIX FORM.

FOR THE LONGITUDINAL PIEZOELECTRIC MODULUS

$$d_{11} = d_{111} \quad \text{IN TENSOR NOTATION}$$

AND THE CHANGE WE ARE MAKING IS TO A $d'_{111} = c_{1q}c_{1m}c_{1n}d_{qmn}$

THE DIRECTION COSINES INVOLVED ARE SIMPLY THE DIRECTION COSINES OF X_1' (WE DON'T CARE ANYTHING ABOUT X_2' AND X_3' AND DON'T NEED THEM!) LET US THEREFORE REPLACE $c_{1q}c_{1m}c_{1n}$ BY MERELY THE DIRECTION COSINES OF THE SINGLE DIRECTION, X_1' WITH WHICH WE ARE CONCERNED AND CHANGE $c_{1q}c_{1m}c_{1n} \rightarrow l_q l_m l_n$.

SO $\boxed{d = d'_{111} = l_q l_m l_n d_{qmn}}$

LET'S DO THIS SUMMATION FOR QUARTZ, POINT GROUP 32

THE FORM OF THE PIEZOELECTRIC MODULUS TENSOR IS

$$d_{ij} = \begin{bmatrix} d_{11} & -d_{11} & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & -d_{14} & -2d_{11} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

BUT THE PROPER FORM OF THE MATRIX WITHOUT EQUALITIES INSERTED IS

$$\begin{bmatrix} d_{11} & d_{12} & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & d_{25} & d_{26} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \qquad \text{WHERE} \begin{cases} d_{22} = -d_{11} \\ d_{25} = -d_{14} \\ d_{26} = -2d_{11} \end{cases}$$

CONVERTING TO A TENSOR (AND MERELY EXTRACTING THE NON-ZERO ELEMENTS

$$d_{111}\ d_{122}\ \underbrace{d_{123}\ d_{132}}\ \underbrace{d_{213}\ d_{231}}\ \underbrace{d_{212}\ d_{221}}$$

NOTE THAT d_{14} IS THE SUM OF TWO MATRIX ELEMENTS

PERFORMING THE TRANSFORMATION

$$\begin{aligned} d'_{111} &= l_1 l_1 l_1 d_{111} + l_1 l_2 l_2 d_{122} + l_1 l_2 l_3 d_{123} + l_1 l_3 l_2 d_{132} \\ &\quad + l_2 l_1 l_3 d_{213} + l_2 l_3 l_1 d_{231} + l_2 l_1 l_2 d_{212} + l_2 l_2 l_1 d_{221} \\ &= l_1^3 d_{111} + l_1 l_2^2 (d_{122} + d_{212} + d_{221}) + l_1 l_2 l_3 (d_{213} + d_{231} + d_{123} + d_{132}) \end{aligned}$$

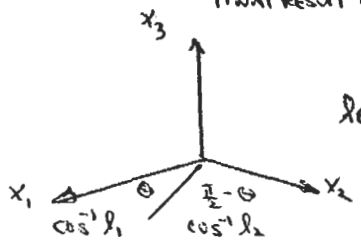
RESTORING MATRIX NOTATION

$$d'_{11} = l_1^3 d_{11} + l_1 l_2^2 (d_{12} + d_{26}) + l_1 l_2 l_3 (d_{25} + d_{14})$$

INSERTING THE EQUALITIES BETWEEN ELEMENTS

$$\begin{aligned} d'_{11} &= l_1^3 d_{11} + l_1 l_2^2 [-d_{11} + (-2d_{11})] + l_1 l_2 l_3 (-d_{14} + d_{14}) \\ &\qquad d_{12} = -d_{11} \quad d_{26} = -2d_{11} \qquad\qquad = 0 \\ &= (l_1^3 - 3 l_1 l_2^2) d_{11} \end{aligned}$$

FINAL RESULT IS $\boxed{d = d'_{111} = (l_1^3 - 3 l_1 l_2^2)\, d_{11}}$ l_3 DOES NOT APPEAR!



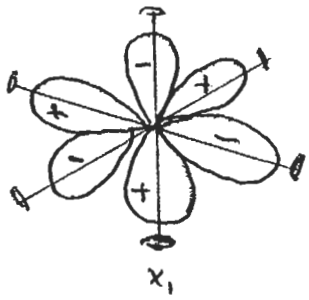
LET $l_1 = \cos\theta$
$l_2 = \sin\theta$

THE IN $X_1 X_2$ PLANE

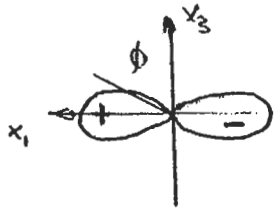
$$d = d_{11} \cos\theta \left(\cos^2\theta - 3\sin^2\theta\right)$$

THIS IS A "WELL KNOWN" (?) IDENTITY

$$\boxed{d = d_{11} \cos 3\theta}$$



NOTE THAT THE SURFACE CONFORMS TO SYMMETRY 32!



IN $X_1 X_3$ PLANE

$$d'_{111} = l_1^3\, d_{11}$$

$$\boxed{d'_{111} = d_{11} \cos^3\phi}$$

THIS IS A UNIVERSAL SURFACE FOR 3RD RANK PROPERTIES FOR SYMMETRY 32!