ADVANCED PHYSICS
LABORATORY
ETH ZURICH

INSTRUCTION NR.

Piezoelectric Effect

Literature, general

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[11] ASHCROFT/MERMIN, Solid State Physics (1976)

Literature on Quartz

[12] A.SCHEIBE, Die Piezoelektrizität des Quarzes

Literature on Barium Titanat

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The bold written text books should be available in the laboratory library.

rev. Mai 2011, Manuel Schneider

Contents

1 Exercises

1. Check the linear relation between force and charge with a sample of quartz at room temperature.

2. Determine the Gauge constant of the apparatus with the well known piezo-module of quartz (literature values) and exercise 1. The Gauge constant has to be specified in CGS and SI units.

3. Verify that the piezo-module of quartz is only slightly temperature dependent.

4. Measure the developing of the piezo-module of Barium Titanate as a function of temperature. Take data for the polarized and the unpolarized sample. Check also the linear relation between force and charge for two fixed temperatures in each case.

5. Analyze how errors arising from the measurement and the regression influence the results on the basis of the data of one measurement.

2 Theory

We give only a short overview about the key aspects of the theory of piezoelectricity in this text. For extensive studies which are absolutely necessary to understand the problem set we refer to the text books.

2.1 Elastic Behavior of Crystals

For any homogeneous medium you can show [5] that an arbitrary deformation can be expressed as a superposition of 6 special, elementary deformations S_i, where $i = 1, \dots, 6$. These are for $i = 1, 2, 3$ the specific longitudinal strains in x-, y- and z-direction; for $i = 4, 5, 6$ the shear strains in the planes parallel to the coordinate axis. The state of stress of a body is described by the (symmetric) stress tensor T_j. The components of the stress tensor are shown in figure 1. S_i and T_j are related by:

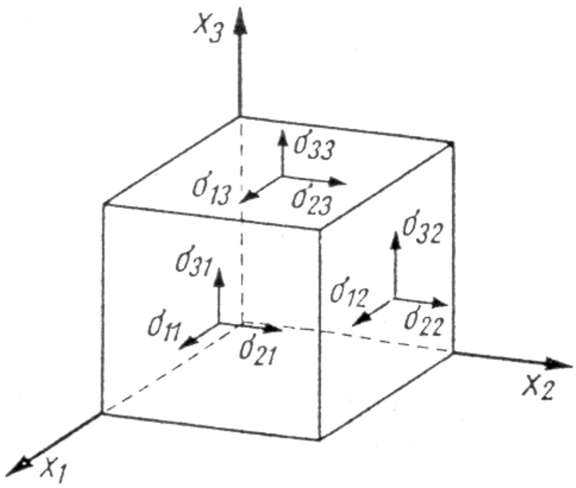

Figure 1: The components of the stress tensor [10].

$$S_i = \sum_{j=1}^{6} s_{ij} T_j \qquad i = 1, \dots, 6 \tag{1}$$

This is the generalization of the common **Hooke's law**. The s_{ij} form the symmetric matrix of the **elastic constants**. The reciprocal relation to (1) is:

$$T_i = \sum_{j=1}^{6} c_{ij} S_j \qquad i = 1, \dots, 6 \tag{2}$$

In this relation the c_{ij} form the also symmetric matrix of the **Young's modulus**. The elastic quantities c and s fulfill the equation:

$$\sum_j s_{ij} c_{jk} = \delta_{ik} \tag{3}$$

Generally, the matrices describing the material properties – in this case s_{ij} and c_{ik} as well as the successively defined d_{ij} and e_{ij} – have to be invariant under the symmetry operations of the respective crystallographic class. This condition leads to the circumstances that the matrices might have a special structure where certain elements are zero or related to each other depending on the crystallographic class. The number of independent constants has its minimum for cubic crystals (only two for the matrices describing the elastic properties as in isotropic matter for example). For the lowest symmetry (triclinic) the number of constants has its maximum, i. e. 21 in case of the elastic constants. The derivation of the structure of these matrices is mostly given by W. Voigt [4]. Tables can be found in the text books.

2.2 The Piezoelectric Effect

Direct Piezoelectric Effect

If you apply a voltage to a certain type of crystals then – besides the elastic deformation – also the center of mass of negative charge is shifted and results in a **volume polarization** P. The necessary and sufficient condition is the absence of inversion symmetry in the crystal lattice. Polarization and state of stress and state of longitudinal strain of the crystal respectively are connected by:

$$P_i = \sum_{j=1}^{6} d_{ij} T_j \qquad i = 1, 2, 3 \tag{4}$$

$$P_i = \sum_{j=1}^{6} e_{ij} S_j \qquad i = 1, 2, 3 \tag{5}$$

d_{ij} and e_{ij} form the matrices of the **piezo modules** and the **piezo constants** respectively. You can find that between the elastic and the piezoelectric quantities the following relation must hold:

$$d_{ik} = \sum_{j=1}^{6} e_{ij} s_{jk} \tag{6}$$

$$e_{ik} = \sum_{j=1}^{6} d_{ij} s_{jk} \tag{7}$$

The connections between deformation and stress and between deformation and electrical polarization are only linear for small deformations. As soon as the displacement of the lattice points is not small anymore compared to the typical lattice distances then terms of higher order arise.

Inverse Piezoelectric Effect

If you place a piezoelectric crystal in an external electric field then a polarization inside the crystal is induced. This polarization results in a deformation of the crystal and therefore in state of stress although no external voltage is applied.

Relation to the Macroscopic Surface Charge

According to the equations of electrostatics a volume polarization is equal to the appearance of a surface charge on the boundary surface of the dielectric. Hence, the system of equations (4) can also be written as:

$$Q_i = \sum_{j=1}^{6} d_{ij} K_j \qquad i = 1, 2, 3 \tag{8}$$

where the Q_i represent the electrical charges on the cross sections of a cubic crystal and the K_j the forces acting on these areas.

2.3 The Piezoelectrical Effect of Quartz

The phase of a quartz crystal (chemical formula: SiO_2) at room temperature belongs to the symmetry group D_{3d} of the trigonal system. Through the symmetry the number of piezoelectric (as well as elastic) constants is considerably reduced. The matrix of the piezo modules has the form:

$$(d_{ij}) = \begin{pmatrix} d_{11} & -d_{11} & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & -d_{14} & -2d_{11} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \tag{9}$$

Quartz thus possesses only two independent piezo modules and piezoelectric constants respectively (the e_{ij}-matrix goes analogically). The orientation of the underlying cartesian coordinate system is shown in figure 2. From (8) and (9) you can see what kind of stress is piezoelectric active and accordingly how a quartz crystal has to be oriented so that the application of a voltage normal to the cross section results in a surface charge. Figure 3 shows the interaction between force, displacement and charge. In this context you should notice that the x, y und z axis do not conform to the crystal axis of quartz. In this experiment a crystal cut in x-direction is put under pressure. In this case equation (8) simplifies to:

$$Q_x = d_{11} K_x \tag{10}$$

2.4 The Piezoelectrical Effect of Barium Titanat

Barium Titanat ($BaTiO_3$) has 4 phases:

above 120°C	cubic
between 120°C und 5°C	tetragonal
between 5°C und –90°C	orthorhombic
below –90°C	rhombohedral

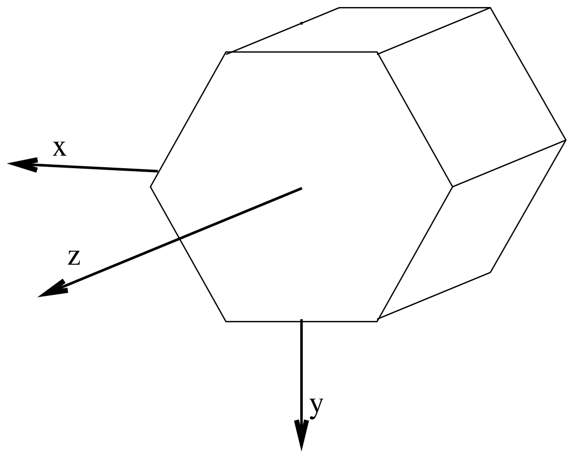

Figure 2: Orientation of the quartz unit cell in the coordinate system of the piezo module matrix. The x-axis coincides with one of the three polar twofold rotation axis and is called electric axis. The y-axis is called neutral axis.

In our experiment we are only interested in the cubic and tetragonal phase. The phases below 120°C are ferroelectric, that is the crystal is spontaneously polarized in these phases without any mechanical pressure. By applying a strong electric field the direction of this spontaneous polarization can be changed (ferroelectric hystereses).

While in the cubic phase (for $BaTiO_3$ it is a primitive lattice) the barium, titanium and oxygen atoms are at the ideal positions of a perovskite structure they are shifted along the z-axis in the ferroelectric tetragonal phase. These displacements amount to:

for Ba:	+5 pm
for Ti:	+10 pm
for O_I:	−4 pm
for O_{II}:	−9 pm

Thereby the center of mass of the negative and the positive charge do not fall together anymore and a spontaneous polarization appears. The cubic phase and the displacements for the tetragonal phase are displayed in figure 4. For this reason the already mentioned condition for a piezoelectric medium is fulfilled, i. e. the absence of an inversion point. So barium titanat is piezoelectric in the tetragonal phase. From this it follows that a ferroelectric medium has to be piezoelectric. The inversion of this rule doesn't have to be true. A piezoelectric medium can but doesn't have to be a ferroelectric.

Since our sample is not a big single crystal but is sintered from a lot of small crystals (ceramic) all possible orientations of the polarization vectors arise during the phase transition from the cubic to the tetragonal phase. Naturally, for such a sample there

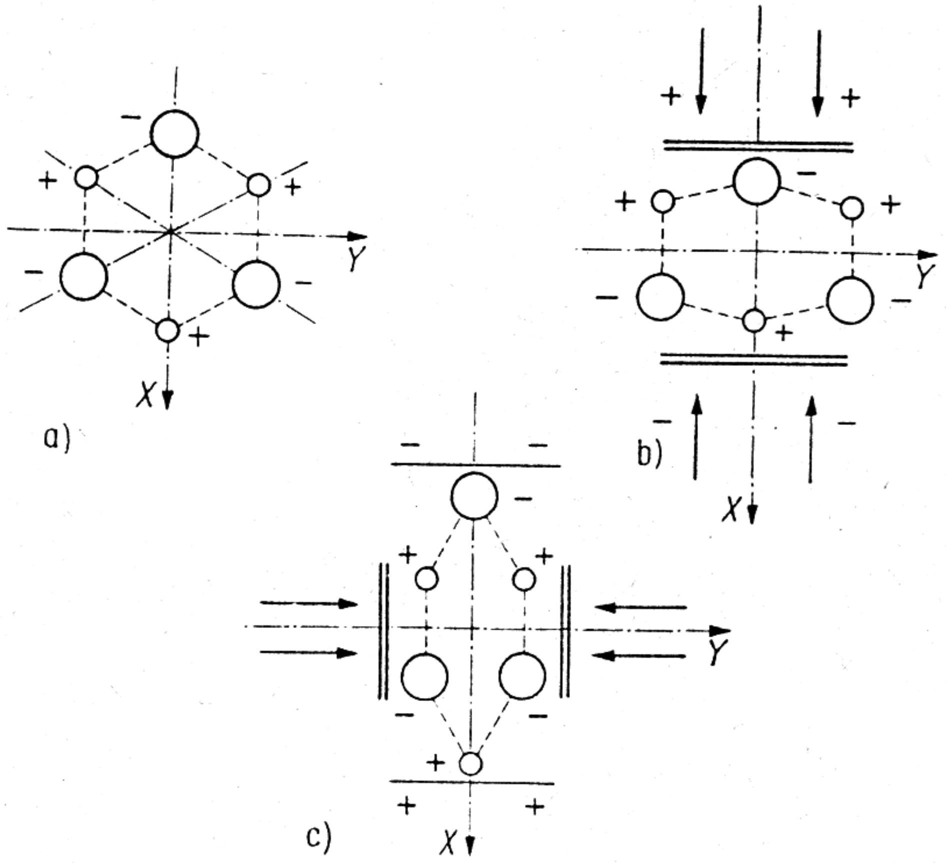

Figure 3: Structural model for the interpretation of the piezoelectric effect of quartz [10].

is no piezoelectric effect. But when an electric field or a mechanical pressure is applied then a favored direction is created and the individual polarization vectors aline more or less. Such a polarized sample shows piezoelectric behavior. The piezo module however is highly dependent on temperature. When heated over 120°C the piezoelectric properties of the crystal disappear. Impurities can smear out the transition point such that we rather have to talk about a transition region.

3 The Measuring Equipment

The sample is placed between two copper blocks (see figure 5). In the lower one there is a copper constantan thermo element which measures the temperature of the sample. The thermo voltage is measured with a compensator (see appendix). The copper blocks are isolated thermally and electrically with two cylinders made of ceramic. The force of a spring is transferred to the crystal over a lever. The transfer ratio of the lever can be varied. The spring connects the lever with an eccentric mechanism which is driven by an electric motor. The test frequency is 5 Hz. The sample and the copper blocks are

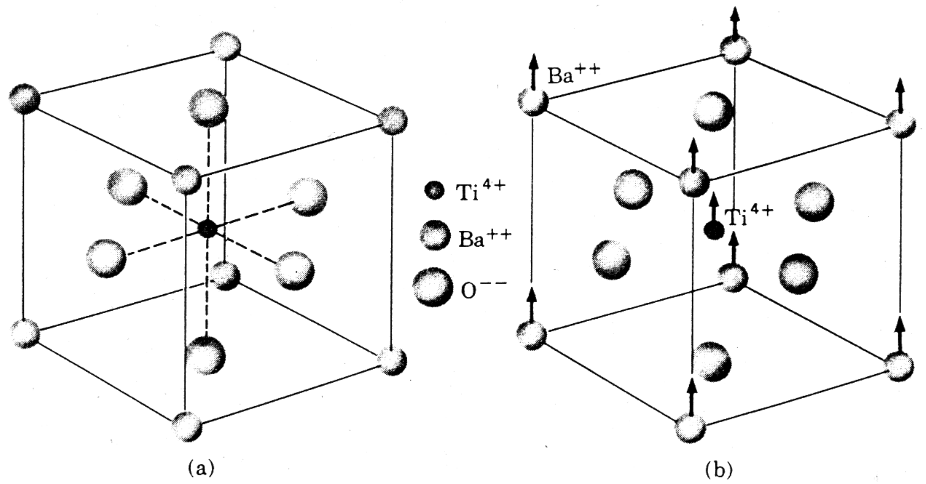

Figure 4: Structure of the cubic barium titanate and direction of the displacements of the lattice points to the tetragonal ferro electric phase.

located in an oven which mustn't be heated over 180°C. The heating coil is separated into two parts which have to be connected in parallel. It adds up to a maximal current of 10 A for an applied voltage of 10 V. To avoid an effect from the current in the heating winding on the crystal one of the two heating coils has to be grounded.
The amplifier and the high voltage source of 1500 V are placed in a separate case which can be connected to the sample with an isolated cabel. Over this cable not only the measurement voltage is brought from the sample to the amplifier but also the high voltage from the electronics to the crystal. There is a switch above the connector on the front of the case which toggles these two functionalities.

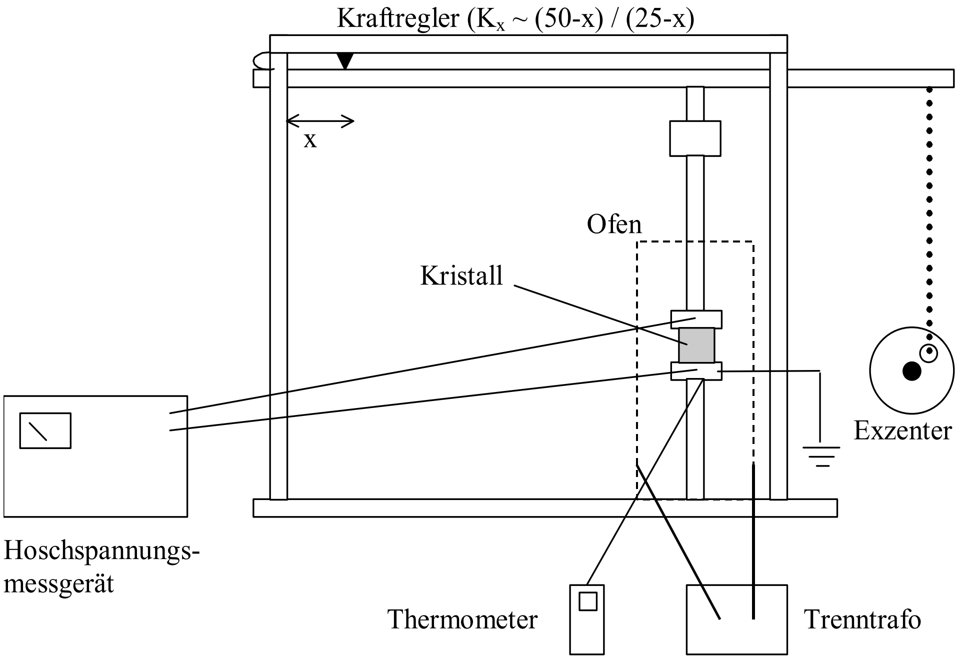

Figure 5: The measuring apparatus.

The following protective measures has to be strictly held:

1. The oven may only be opened if
   a) power switch of the electronics is switched off;
   b) the toggle for measurement – high voltage is on the neutral, middle position.
2. Also the cable between the electronic and the mechanical part may only be unplugged if 1a) and 1b) are fulfilled.
3. The electronic case, the metal parts of the mechanics and the heating coils have to be grounded.
4. The maximal heating rate of the oven is 30°C/hour. It is also strictly forbidden to open the oven while it is still hot or to speed up the cooling with compressed air, water etc.
5. Pay attention that the sample lays always flat on the copper blocks. It may break otherwise.

The input impedance of the amplifier consists of a 45.5 MΩ resistance and a 180 nF capacitor in parallel. Since the impedance of a 180 nF capacitor is small for a frequency of 5 Hz compared to the total impedance:

$$|Z_C| \;=\; \frac{1}{\omega C} \;=\; \frac{1}{2\pi \cdot 5\,\mathrm{Hz} \cdot 180\,\mathrm{nF}} \;=\; 0.16\,\mathrm{M\Omega}\,, \tag{11}$$

most of the current is going into the capacitor. With the capacitor equation

$$Q \;=\; C \cdot V \tag{12}$$

equation (10) becomes:

$$d_{11} \cdot K_x \;=\; C \cdot V_x \tag{13}$$

If there is a force varying with time acting on the crystal then also the volume polarization changes constantly and generates an electric current. For the experiment we have a periodic force $K_0 \cdot \cos(\omega t + \varphi)$ and a lever which transfers the force from the motor to the sample. The force K_x acting on the crystal then is:

$$K_x \;=\; \frac{50 - x}{25 - x} \cdot K_0 \cdot \cos(\omega t + \varphi) \tag{14}$$

This results in a current with

$$V_x \;=\; d_{11} \cdot \frac{K_x}{C} \;=\; d_{11} \cdot \frac{50 - x}{25 - x} \cdot \frac{K_0 \cdot \cos(\omega t + \varphi)}{C} \tag{15}$$

When we call the amplification factor of the apparatus $g = 1/R$ and take the rectifier into account (time average of $\cos(\omega t + \varphi)$) we then get an outgoing direct current

$$I \;=\; d_{11} \cdot \frac{g \cdot \langle K_x \rangle}{C} \tag{16}$$

The Gauge constant $\eta_g = 1/C$ of the apparatus is given by

$$\eta_g \;=\; \frac{I}{\langle K_x \rangle} \cdot \frac{1}{d_{11} \cdot g} \tag{17}$$

Since the measured current I doesn't have to be zero although no force is acting on the sample you better take $\Delta I / \Delta \langle K_x \rangle$ instead of $I / \langle K_x \rangle$ to avoid an additive constant. This is possible thanks to the linear relation between force and charge. When you make a linear regression of the measured data you get for the Gauge constant

$$\eta_g \;=\; \frac{\mathrm{d}I_{eff}}{\mathrm{d}K_x} \cdot \frac{1}{d_{11} \cdot g} \tag{18}$$

and for the piezo module

$$d_{11} \;=\; \frac{\mathrm{d}I_{eff}}{\mathrm{d}K_x} \cdot \frac{1}{\eta_g \cdot g} \tag{19}$$

4 The Measurements

Never touch the crystals with bare hands. This may influence the results (we measure surface charge!). Since you cannot be sure that the crystals are clean you should clean them with alcohol before taking the measurements. Do the cleaning with cotton gloves.

To determine the piezo module for a fixed temperature you best measure the current I for different forces K_x. The force can be modified by changing the transfer ratio.

For the measurements on barium titanat you should use the scheme shown in figure 6. It is quite tempting to take the first measurements of the unpolarized barium ti-

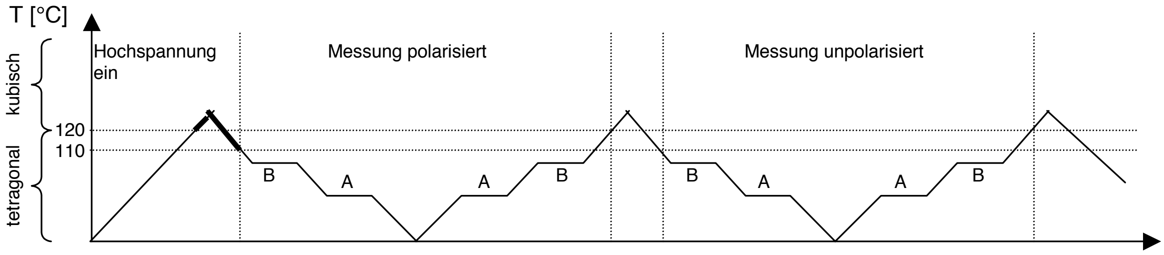

Figure 6: The horizontal parts A and B denote the measurements for the linear relation at constant temperature. Attention: When you turn off the oven the temperature is not constant immediately but can still go up or fall a few degrees.

tanat during the first heating phase but this can lead to errors. Through the pressure of the copper plates on the crystal and the usually long time during which it is unused (a few days are enough) the barium titanate can get polarized which it mustn't be. This polarization is much smaller than the one arising from the high voltage but can still be measured and gives a data curve that looks quite similar to the polarized barium titanate. Therefore it is recommended to take the measurements shortly after each other.

5 Applications of the Piezoelectrical Effect

You will see from the measurements that quartz has an almost temperature independent piezoelectric effect. Therefore quartz is highly applicable to force measurements. On the other hand quartz can be excited to mechanical oscillations by an electric field naturally. For this it is important that the thermal expansion is very small. Thus the mechanical resonance of quartz changes only slightly with temperature such that an oscillating crystal is a good frequency standard. Ferro electrical matter such as $BaTiO_3$, $PbTiO_3$ etc. has a bigger piezo module. They can be used where a very high sensitivity is recommended like in crystal pick-ups of record players, crystal microphones or gas lighters. But such transformers are not very stable and change their properties with temperature and time.

Appendix: measuring amplifier 5 Hz piezoelectric effect