Piezo-quasi-mosaic effect in x-ray diffraction

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The increase in the intensity of the x-ray reflection from single-crystal quartz plates placed between capacitor electrodes under a dc voltage ($U_0/L = 50$–100 kV/cm), previously observed by Kakiuchi (Phys. Rev. **54**, 772 (1938), is investigated by us in greater detail and directly in the geometry of a two-crystal x-ray spectrometer or of a Cauchois-system focusing x-ray spectrometer. The main properties of the phenomenon observed by Kakiuchi are confirmed and a model is proposed for it. A study is made also of the joint influence exerted on the diffraction process by the elastic quasi-mosaic effect (O. I. Sumbaev, Crystal-Diffraction Gamma Spectrometers [in Russian], Gosatomizdat, 1963; Sov. Phys. JETP **27**, 724, 1968) and of the phenomenon in question, an action that can be called piezo-quasi-mosaic effect. A substantial increase of the luminosity of diffraction x-ray spectrometers (approximately fivefold with a Cauchois system and by a factor 20–30 when the two-crystal variant is used) is shown to be attained under certain conditions as a result of the piezo-quasi-mosaic effect.

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INTRODUCTION

The diffraction of radiation by crystals depends strongly on the parameter that characterizes the width of the distribution with respect to the angles of the individual blocks of the single crystal. For example, in the so-called thick-crystal region this parameter is proportional to the integrated reflection coefficient, i.e., to the area of the diffraction line. For the most perfect single crystals (quartz, calcite, germanium, silicon), the width of the distribution of the mosaic blocks in angle can be of the order of fractions of a second, whereas, for example, in the pyrolitic graphite used to monochromatize thermal neutrons this parameter is raised artificially to a value on the order of ten minutes, thereby exceeding the minimum attainable value by three orders of magnitude. The intensity of the reflected beam can accordingly also increase by thousands of times.

The production of a single crystal with a specified mosaic structure, however, is a most complicated technological problem. Furthermore, it is important in a number of cases to maintain a maximally high homogeneity of the properties over the area of the plate, a property typical of crystals closest to ideal, but lost when an attempt is made to increase the mosaic blocks during the growth, for example by artificially introducing impurities or dislocations. A possible way out might seem to be the use of effects inherent in ideal crystals, i.e., those having the maximum degree of homogeneity over the plate area, but imitating at the same time the mosaic structure.

This has prompted us to continue a search for effects of this type, similar to the elastic quasi-mosaic effect,[2,3] and to investigate in greater detail the phenomenon described in a short letter by Kakiuchi[1] back in 1938. Some results of this investigation are in fact the subject of the present article.

THEORY OF THE EFFECT

Consider a plane-parallel single-crystal α-quartz plate of thickness L, cut in such a way that the crystallographic planes (hkl) coincide with the normal cross sections of the plate. Let the plate be placed between capacitor electrodes to which a dc voltage is applied (see Fig. 1a). We shall derive an expression for the shapes of the (hkl) planes under conditions of the inverse piezoeffect and consider the diffraction of x rays from these planes.

We confine ourselves for simplicity to the one-dimensional planar problem. The distribution of the potential over the thickness of such a plate $V(y)$, in the absence of free charges inside the dielectric is obviously given by

$$V(y)=U_0y/L, \quad L\geqslant y\geqslant 0. \tag{1}$$

If, on the other hand, we follow Ioffe[4] and assume that application of an electric field to the quartz leads to formation of charge layers near the corresponding electrodes, then the distribution of the potential over the thickness of the plate can be described with the aid of a model, by approximating Ioffe's experimentally obtained relation by a function of the type[1)]

$$V(y)=U_0y/L+b\sin(2\pi y/L). \tag{2}$$

We then obtain for the field intensity $E(y)$ in the crystal

$$-E(y)=\frac{dV(y)}{dy}=\frac{U_0}{L}+b\frac{2\pi}{L}\cos\frac{2\pi}{L}y. \tag{3}$$

We put also

$$E(y)|_{y=L/2}\approx 0. \tag{4}$$

Hence $b=U_0/2\pi$, and then

$$V(y)=U_0\left(\frac{y}{L}+\frac{1}{2\pi}\sin\frac{2\pi}{L}y\right), \tag{5}$$

$$-E(y)=\frac{U_0}{L}\left(1+\cos\frac{2\pi}{L}y\right). \tag{6}$$

It follows from $\operatorname{div}\mathbf{E}=4\pi\rho$, where ρ is the space charge, that

$$\rho(y)=\frac{U_0}{2L^2}\sin\frac{2\pi}{L}y. \tag{7}$$

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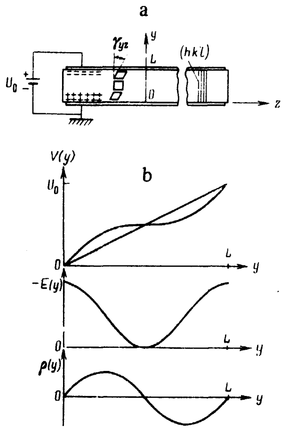

FIG. 1. a) Quartz plate with reflecting planes (hkl) in an electric field; b) distributions of the potential $V(y)$, of the field intensity $E(y)$, and of the charge $\rho(y)$ over the plate thickness.

The obtained plots of $V(y)$, $E(y)$ and $\rho(y)$ are shown in Fig. 1b.

If the plate placed in an electric field has piezoelectric properties, then the inverse piezoelectric effect produces in it mechanical strains γ_{ik} proportional to the field intensity. These strains are described by an equation of the type

$$\gamma_{ik}=d_{ikl}E_l,$$

where d_{ikl} is the piezoelectric-coefficient tensor. In the case of a one-dimensional planar problem, there is present only on field component E_y and the strains that influence directly the shape of the (hkl) plane are shear strains, namely[2)]

$$\gamma_{yz}=d_{24}E_y=-d_{24}\frac{dV(y)}{dy}. \tag{8}$$

Figure 1a (left) shows a chain of rectangles deformed by the field, and explains the character of the deformation of the plane. The equation $z=f(y)$ of this surface in terms of the coordinates of our problem can be easily obtained by recognizing that, by definition, $\gamma_{yz}=dz/dy$. It follows from (8) that

$$\frac{dz}{dy}=-d_{24}\frac{dV(y)}{dy}, \tag{9}$$

whence we obtain for the equation of the surface

$$z=-d_{24}V(y)+C, \tag{10}$$

where C is an integration constant. Thus the sought shape of the originally plane surface that has become bent in the inhomogeneous electric field is similar to the function $V(y)$ considered above.

If the tensor component d_{24} vanishes, then $z=C$, i.e., the cross section of the plate is not deformed in the electric field. The tensor component d_{24}, on which the deformation of the surface depends, can be calculated for a plane of any orientation by using the usual transformation rules and starting from the known principal values of the piezoelectric coefficients. The results of such calculations for quartz are given, for example, in Cady's book. Figure 2 shows values of the piezoelectric coefficient d_{24} for α-quartz cuts usually employed in crystal-diffraction x-ray spectrometers operating in transmission. It is seen that this coefficient depends on the rotation of the cut around an axis perpendicular to the chosen reflecting plane, and this dependence illustrates the possibility of obtaining plates having the same and identically oriented (i.e., normal reflecting) planes, but with different values of the coefficient d_{24} that is responsible for the effect.

We proceed to consider the diffraction of x rays by a crystal whose reflecting surfaces have a shape described by Eq. (10). We introduce the function

$$W_{\rm pl}(\vartheta-\vartheta_{\rm Br})\equiv W_{\rm pl}(\varepsilon)=\frac{1}{L}\left|\frac{dy}{d\varepsilon}\right|, \tag{11}$$

which is the relative fraction of the plate thickness per unit diffraction angle. For an ideal crystal with flat planes it is obvious that

$$W_{\rm pl}(\varepsilon)=0 \quad \text{if} \quad \varepsilon\neq0, \qquad W_{\rm pl}(\varepsilon)\to\infty \quad \text{if} \quad \varepsilon=0, \tag{12}$$

with

$$\int_\varepsilon W_{\rm pl}(\varepsilon)d\varepsilon=\frac{1}{L}\int_0^L dy=1, \tag{13}$$

i.e., $W_{\rm pl}(\varepsilon)$ for this crystal is a delta-function.

A real, i.e., mosaic crystal is characterized by a distribution function $W_g(\varepsilon)$ of the block mosaic-angles. $W_g(\varepsilon)$ is usually assumed Gaussian. The width ω_g of this distribution is 0.5–1" for the most perfect crystals. The over-all distribution $W_\Sigma(\varepsilon)$, due to the bending of the reflecting planes and to the natural mosaic structure, is described by the convolution of the corresponding distribution functions

$$W_\Sigma(\varepsilon)=\int W_g(\varepsilon')W_{\rm pl}(\varepsilon-\varepsilon')d\varepsilon'. \tag{14}$$

In the case of a mosaic crystal with flat reflecting planes we have

$$W_\Sigma(\varepsilon)=\int W_g(\varepsilon')\delta(\varepsilon-\varepsilon')d\varepsilon'=W_g(\varepsilon), \tag{15}$$

i.e., the summary angular distribution of the mosaic

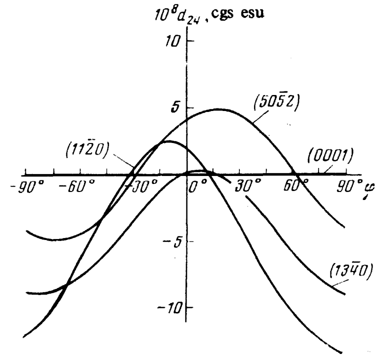

FIG. 2. Calculated values of the piezoelectric coefficient d_{24} for quartz plates with different reflecting planes, as functions of the rotation of the cut.[5]

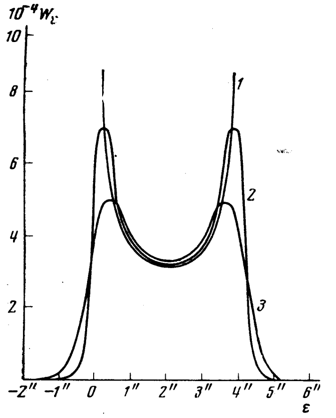

FIG. 3. Distribution W_Σ with respect to the mosaic block angles at $\Phi = 2U_0 d_{24}/L = 4''$, curve 1—ideal crystal, $\omega_g = 0$; curve 2—mosaic crystal, $\omega_g = 0.5''$; curve 3—mosaic crystal, $\omega_g = 1''$.

structure naturally coincides in such a crystal with the distribution with respect to the mosaic-block angles.

At low deformations of the crystal in the electric field, the following relation is valid

$$\varepsilon \approx \gamma_{yz} = \frac{dz}{dy}, \tag{16}$$

and for W_{pl} we obtain in this case

$$W_{pl}(\varepsilon) = \frac{1}{L}\left|\frac{dy}{d\varepsilon}\right| = 1 \Big/ L\left|\frac{d^2z}{dy^2}\right|. \tag{17}$$

Using (10), we get

$$W_{pl}(\varepsilon) = \left(Ld_{24}\left|\frac{d^2V(y)}{dy^2}\right|\right)^{-1}. \tag{18}$$

Changing over to a model representation of the potential (5) and taking (13) into account, we have

$$W_{pl}(\varepsilon) = \frac{1}{\pi}\left[\varepsilon\left(\frac{2d_{24}U_0}{L} - \varepsilon\right)\right]^{-1/2}, \quad 0<\varepsilon<2\frac{U_0}{L}d_{24}. \tag{19}$$

The form of W_{pl} is shown in Fig. 3, curve 1; curves 2 and 3 show the course of the summary mosaic structure $W_\Sigma(\varepsilon)$, calculated for formula (14) with $2d_{24}U_0/L = 4''$ and $\omega_g = 0.5''$ and $1''$, respectively.

The diffraction of the x rays by such a crystal is substantially altered. In this sense, the effect if analogous to the elastic quasi-mosaic effect[2] and can be named piezo-quasi-mosaic. In fact, using the expression derived for the reflection coefficient within the framework of the model of an ideal mosaic crystal[6]

$$\begin{gathered} I(\vartheta-\vartheta_{Br}) \\ = \frac{1}{2}\left[1 - \exp\{-2RW_\Sigma(\vartheta-\vartheta_{Br})\}\right], \\ R = \frac{P^2}{\cos^2\vartheta} r_0^2 \left(\frac{F}{\Omega}\right)^2 \lambda^2 Ld, \end{gathered} \tag{20}$$

where $I(\vartheta - \vartheta_{Br})$ is the coefficient of reflection of radiation incident at an angle ϑ from the crystal; P is a factor that takes the polarization of the incident radiation into account; r_0 is the classical radius of the electron; F is a structure factor; Ω is the volume of the unit cell of the crystal; λ is the wavelength of the diffracted radiation; and d is the distance between the reflecting planes, we can quantitatively evaluate the influence of piezo-quasi-mosaic effect on the x-ray diffraction.

If the condition

$$2RW_\Sigma(\vartheta-\vartheta_{Br}) \geqslant 2RL/\pi d_{24}U_0 \gg 1 \tag{21}$$

is satisfied ($L/\pi d_{24}U_0$ is the value of W_Σ at the minimum), then the reflection coefficient is maximal in the entire region $0<\varepsilon<2U_0 d_{24}/L$ and is equal to 1/2 (the region of the so-called thick mosaic crystal). The integrated reflection coefficient, i.e., the area under the line

$$R_i \approx U_0 d_{24}/L + \omega_g/2, \tag{22}$$

then increases in proportion to the average field intensity U_0/L, and also in proportion to the piezoelectric-tensor component d_{24}, and can be several times larger than usual. For example, assuming $L = 1$ mm, $U_0 = 3000$ V, and using the value of d_{24} for a quartz plate cut so that the optical axis is parallel to the lateral edge and the reflecting planes $(13\bar{4}0)$ coincide with the normal cross sections, we get

$$\Phi = 2U_0 d_{24}/L = 18\cdot 10^{-6} \approx 3.6''$$

(Φ is the width of the piezo-quasi-mosaic block). Accordingly,

$$R_i/R_g = \Phi/\omega_g \approx 6 \quad \text{for} \quad \omega_g \approx 0.7''.$$

This gain can be particularly substantial if a two-crystal diffraction spectrometer is used, where the area of the line is proportional to the product of the integrated coefficients of reflection from each crystal, and can increase in the considered effect by a factor $(\Phi/\omega_g)^2$.

DESCRIPTION OF EXPERIMENT AND RESULTS

The experimental investigation of the effect of the piezo-quasi-mosaic structure on x-ray diffraction from perfect quartz single crystal was carried out with a two-crystal spectrometer of the Laue–Laue type, as well as with a Cauchois-type focusing spectrometer. The latter made it possible to study the joint influence on the diffraction of the investigated effect and of the effect of the elastic quasi-mosaic structure.

A diagram of the two-crystal spectrometer is shown in Fig. 4a. The x rays from the anticathode of the x-ray tube RT (Mo anticathode—$U_a = 40$ kV, $I_a = 20$ mA), after passing through a collimator Coll 380 mm long with a slit 1×20 mm, strikes a plane-parallel plate C_1 cut from a natural α-quartz single crystal. The radiation diffracted by this crystal is additionally reflected by the crystal C_2 and is registered by scintillation detector D. The crystal units were assembled on OT-02M theodolites, thereby ensuring that the relative rotation of the crystal could be read accurate to ~0.5''. The crystals were equipped with electrodes of aluminum foil 25 μm thick, connected to a dc voltage source. The working reflecting planes in crystals C_1 and C_2 were the $(13\bar{4}0)$ planes. The dimensions of the crystals and the orienta-

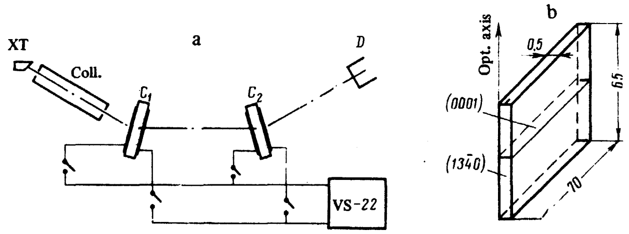

FIG. 4. Diagram of two-crystal x-ray spectrometer (a). Crystal dimensions and orientation of the reflecting plane relative to the optical axis of the monoblock (b).

tion of the reflecting planes relative to the optical axis of the monoblock are shown in Fig. 4b.

In the first experiment we studied the dependence of the number of counts at the maximum of the two-crystal $K_{\alpha 1}$ line of Mo on the time reckoned from the instant when a voltage $U_0 = 3400$ V was applied simultaneously to both crystals. The maximum value of the ratio $N(3400\text{ V})/N(0)$, determined by the saturation of the curve, was ~32. The time at which the curve reached saturation (about two hours) characterizes the time required for the formation of the charge layers in the crystals.

From a comparison of the shape of the line obtained at saturation ($U_0 = 3400$ V) with the line shape at $U_0 = 0$ (Fig. 6) it is seen that these lines, while differing greatly in intensity, have practically equal half-widths. Thus, no loss takes place in the energy resolution of the apparatus under these conditions when the effect of the piezo-quasi-mosaic structure is measured with a two-crystal x-ray spectrometer.

To prove the dependence of the effect on the value of the piezoelectric coefficient d_{24} an experiment was performed, in which the intensities of the reflections from the planes (13$\bar{4}$0) ($d_{24} = 9 \cdot 10^{-8}$ CGSE) and (0001) ($d_{24} = 0$) of the same crystal C_1 were compared (see Fig. 4b). The voltage on crystal C_1 was 3400 V, and that on crystal C_2 zero. Figure 5 shows plots of the changes in the counts at the maximum of the two-crystal line as a function of the time after application of the voltage, in the case of reflection from the compared planes. As expected (see relation (22)), the increase of the intensity is clearly seen for the reflecting (13$\bar{4}$0) planes and is nonexistent for the (0001) planes.

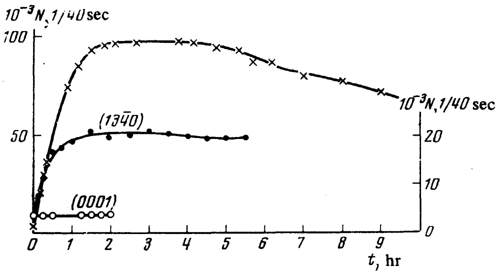

FIG. 5. Dependence of the intensity at the maximum of the two-crystal line on the time elapsed from the instant when a voltage $U_0 = 3400$ V is turned on: ×—voltage on both crystals, left-hand scale; ●—voltage on crystal C_1, reflecting planes (13$\bar{4}$0), right-hand scale; ○—voltage on crystal C_1, reflecting planes (0001), third order of reflection, right-hand scale.

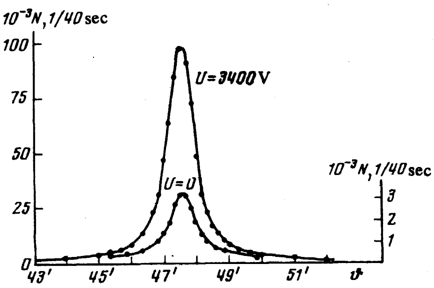

FIG. 6. K_α x-ray line of Mo, obtained with two-crystal spectrometer at a voltage $U_0 = 3400$ V on both crystals (left-hand scale) and at $U_0 = 0$ (right-hand scale), ϑ—angle of rotation of crystal.

To investigate the joint action exerted on x-ray diffraction by the elastic-quasi-mosaic effect and by the piezo-quasi-mosaic effect, as well as to answer the important question whether the investigated effect can be used to increase the luminosity of focusing spectrometers, two quartz plates with (13$\bar{4}$0) reflecting planes and with respective reflecting surface flexure coefficients[2] $K_1 \approx 0$ and $K_2 = 2 \times 10^{-4}$ cm^{-1} were alternately clamped in the crystal holder of a Cauchois-system focusing diffraction spectrometer. For each plate we investigated the dependences of the intensity on the maximum of the Mo K_{α_1} diffraction line on the magnitude and polarity of the voltage U_0 applied to the electrodes. These dependences are plotted in Fig. 7, curves 2 and 4 being obtained after rotating the investigated plate in the crystal holder 180° about an axis perpendicular to the reflecting planes (the direction of the field relative to the crystal holder remained unchanged). This rotation reverses the direction of the flexure of the reflecting planes of the crystal due to the elastic quasi-mosaic structure, leaving unchanged the flexure due to the piezo-effect. For the plate with $K = 2 \times 10^{-4}$ cm^{-1} (Fig. 7, curves 1 and 2), the angle width of the elastic quasi-mosaic ω_{qu} is[2]

$$\omega_{qu} = 2KL = 8'',$$

$L = 1$ is the plate thickness.

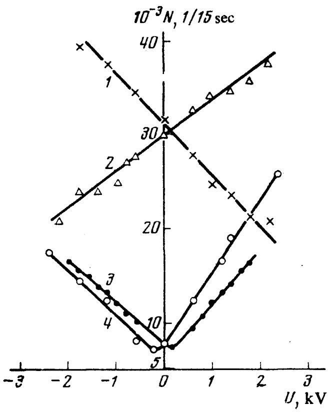

FIG. 7. Dependence of the maximum of the MoK_α line intensity, obtained with a Cauchois-system focusing spectrometer, on the magnitude and polarity of the voltage on the crystal electrodes. Curves 1 and 2—crystal with $K = 2 \times 10^{-4}$ cm^{-1}, curves 3 and 4—crystal with $K \approx 0$.

The action of a field of given sign on such a plate consists of either increasing the existing curvature of the reflecting surfaces via the piezo-quasi-mosaic effect, and thus substantially increasing the diffraction line intensity, or conversely of compensating in part for the elastic flexure of the reflecting surfaces, as is manifest by a decrease in the line intensity. At small widths of the quasi-mosaic blocks, $K \approx 0$ (Fig. 7, curves 3 and 4), the compensation can cause the curvature of the surface to reverse sign so that the subsequent diffraction is governed mainly by the piezo-quasi-mosaic effect, i.e., when the voltage on the crystal is increased the line intensity goes through a minimum and then increases, as is observed in experiment.

Experiments performed with a focusing spectrometer confirm decisively that the piezo-quasi-mosaic effect, just as the elastic quasi-mosaic effect, constitutes a directional and ordered flexure of the reflecting surfaces. Otherwise, assuming a statistical disorientation of the blocks of the crystal in the electric field,[1] it would be impossible to explain the decrease of the diffraction-line intensity, since the superposition of the statistic distribution on the distribution governed by the flexure of the reflecting surfaces would always lead to an increase of the summary distribution, and hence to an increase of the line intensity.

As to practical applications, the elastic quasi-mosaic effect makes it possible to choose, when the plate is made, the desired operating point of the focusing-spectrometer crystal (a constant value of the quasi-mosaic structure for the given plate), while the piezo-quasi-mosaic effect permits a smooth variation of the quasi-mosaic width so as to optimize the diffraction conditions directly during the course of the measurements.

We note in conclusion that the piezo-quasi-mosaic effect can be used also in diffraction of neutrons by perfect piezoelectric single crystals. One can count on readily attaining and satisfying the thick-crystal condition (relation (21)) in diffraction of thermal neutrons ($\lambda \approx 2$ Å), say at millimeter thicknesses for quartz plates. Thus, if a resolution (a "line" width) of several seconds of angle is sufficient, then the luminosity of a two-crystal neutron spectrometer (see, e.g.,[7]) can be appreciably increased. Finally, the indicated effect can be used to record information in single crystals.[8]

The authors thank A. I. Smirnov for designing and constructing the two-crystal x-ray spectrometer used in the measurements.

[1)] Free carriers are present in a real crystal as a result of impurities or faults, and can also be produced by temperature or ionizing radiation.

[2)] The shape of the reflecting plane can also be affected by the strains $\gamma_{zz} = d_{23} E_y$. At $E_y = f(y)$, the individual layers tend to stretch (contract) differently, i.e., they influence one another, and the problem then becomes more complicated.

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