11
X – RAYS AND X – RAY ORIENTATION

INTRODUCTION

We have seen in Chap. 8 that the frequency-temperature characteristics of a vibrating quartz piezoid depend on its orientation with respect to the crystallographic axes. In particular, Eq. (92) shows that the frequency-temperature coefficient T_f for the rotated Y-cut family which includes the AT- and BT-cuts is a function of the angle θ which is the angle between the plane of the quartz blank and the Z-axis. (The angle θ is often called the ZZ' angle.) Figures 8.3 to 8.5 show how T_f is affected by changes in the angle θ. For example, from Fig. 8.3 we see that a 100 MHz AT-cut plate with a ZZ' angle of 35°26′ exhibits a frequency change of only ± 12 ppm over a temperature range of −60 to +100°C. The frequency excursion is doubled if the ZZ' angle is increased or decreased by only 4′.

It is apparent that precise control of the angle of orientation is required in order to take advantage of the inherent temperature stability of the quartz crystal resonator. Other factors, including the electrode material and thickness, the dimensions and contour of the blank, and mounting stresses also influence the frequency-temperature characteristics, but the dominant factor is the orientation.

Before the development of x-ray diffraction equipment, quartz piezoids were oriented by reference to the natural faces of the crystal. For example, an AT-cut can be made by sawing a blank, making a dihedral angle of about 3° with respect to a minor rhomb (r) face of the natural crystal; the line of intersection of the two planes is the X-axis. This is readily seen from Fig. 8.2, where it is shown that the r face makes an angle of 38°13′ with the Z-axis

and the AT-cut makes an angle of about 35° 15′ (the exact angle depending on the application) with the *Z*-axis.

Using crystals with well-developed natural faces, and with skill and care, it is possible to cut blanks with an accuracy of perhaps ±30′. However, in the absence of good natural faces and where greater precision is required, x-ray diffraction methods are necessary. Without x-ray diffraction it would be quite impossible to achieve the precision required in most applications of piezoelectric resonators. It is interesting to note that the first commercial application of x-ray diffraction was made in the quartz crystal industry during the years of World War II.

NATURE AND PRODUCTION OF X-RAYS

X-rays are very short electromagnetic waves. They are produced when electrons traveling at high velocities strike a stationary atom. An x-ray tube is a high vacuum diode having a hot filament or cathode which provides a supply of electrons, and an anode or target upon which the electrons impinge. The x-ray tubes used in the quartz crystal industry always have copper targets. The reason for this will appear later. The anode must be at a high positive potential with respect to the cathode. Some tubes are operated on alternating current. In this case the tube acts as a rectifier and x-rays are produced only during that part of the cycle during which the anode is positive relative to the cathode. Currents of 1 to 50 mA are commonly employed. The anode may be either air- or water-cooled.

The spectrum of x-rays emitted by the target consists of a continuous range of wavelengths (Bremsstrahlung) with the shortest wavelength depending on the peak voltage across the tube and the longest wavelength depending on the material of the window of the tube. In addition to the continuous spectrum, often called *white radiation*, the tube emits intense radiation of discrete wavelengths (provided the voltage is high enough) which depends upon the atoms of which the target is made. The strongest of these characteristic radiations is called the $K\alpha_1$ radiation or wavelength. Very close to it in wavelength and about half as intense is another line called the $K\alpha_2$ radiation. Another pair of lines of somewhat shorter wave-

length and about 15 percent the intensity is called the $K\beta_1$ and $K\beta_2$ radiation. The manner in which the intensity of the radiation from a copper target varies with wavelength at two different voltages is shown in Fig. 11.1. At voltages lower than about 8 kV the $K\alpha$ radiation is not excited. Any voltage greater than this threshold voltage may be used to produce the $K\alpha$ radiation, but in order to obtain adequate intensity, voltages of 25 to 50 kV are commonly employed. The wavelength of the characteristic radiation does not depend on the voltage or the current or even the temperature but only on the atoms of which the target is made. It thus provides a fixed standard of length for making measurements.

The wavelengths of the characteristic radiations have been carefully determined and the values for copper are given in Table 11.1.

BRAGG DIFFRACTION

A beam of x-rays incident on a crystal may be scattered coherently if certain conditions are met. This coherent scattering is often called *reflection*, although unlike optical reflection, it can occur only at specific angles. Sometimes the word *diffraction* is used, but this term is not strictly applicable either, at least in the optical sense. We will use the term *reflection* with the understanding that we refer to the phenomenon of coherent scattering from the atomic planes of a crystal.

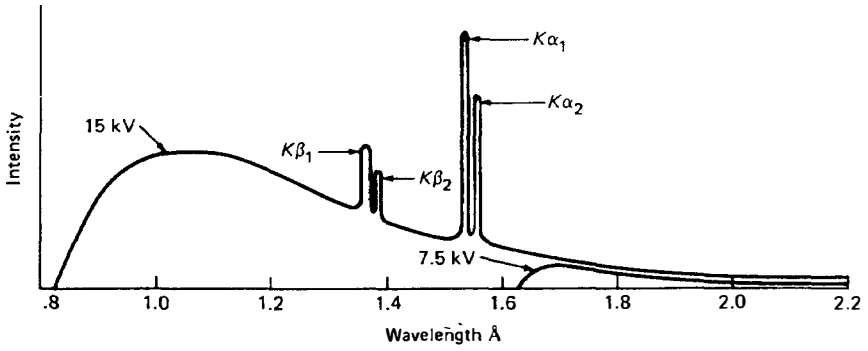

Fig. 11.1. Variation of the intensity of the radiation from a copper target at 7.5 and 15 kV. The intensity is not shown to scale; the characteristic intensities are relatively much greater.

Table 11.1. Characteristic Wavelengths for Copper.

$K\alpha_1$ = 1.537395 A	$K\beta_1$ = 1.38935 A
$K\alpha_2$ = 1.541232	$K\beta_2$ = 1.37824

Note: x-ray wavelengths are often given in XU. One A is equal to 1×10^{-8} cm and 1000 XU = 1.00202 A. The difference is not important for our purposes.

The condition for coherent scattering or reflection of x-rays from a crystal is known as the Bragg relation, which is written

$$n\lambda = 2d \sin \theta_B \qquad n = 1, 2, 3, \ldots \tag{105}$$

where λ = wavelength of the x-rays
d = distance between planes of atoms in the crystal
θ_B = angle (called *Bragg angle*) at which reflection occurs

The integer n is called the order of the reflection. Usually n is not greater than 3.

The origin of the Bragg relation is easily seen from Fig. 11.2. The horizontal rows of dots represent planes of atoms separated by the distance d. A beam of monochromatic x-rays of wavelength λ is incident from the left. In order for this beam to be reflected coherently (diffracted), the path difference $AB - AC$ must be equal to an integral number of wavelengths. But $AB = d/\sin\theta$ and $AC = AB \cos 2\theta$. Therefore

$$n\lambda = AB - AC = \frac{d}{\sin\theta} - \frac{d\cos 2\theta}{\sin\theta} = 2d \sin\theta$$

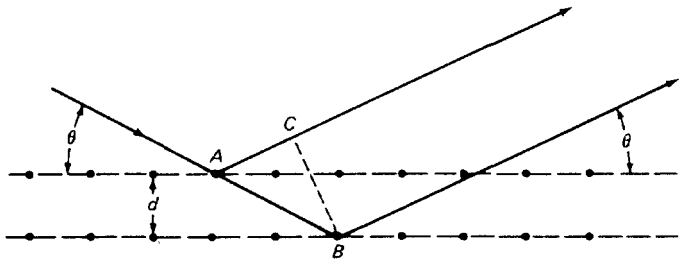

Fig. 11.2. The origin of the Bragg relation.

It must be remembered that x-ray reflection, unlike optical reflection, does not occur from the surface but from planes of atoms which may or may not be parallel to the surface of the specimen. This reflection involves the first few hundred atomic planes. It should also be noted that the angle of reflection, i.e., the Bragg angle θ_B, is always taken to be the angle between the incident beam and the reflecting planes in contrast to the custom in optical work where the angle of incidence is defined to be the angle between the incident beam and the *normal* to the reflecting surface.

It follows from the Bragg relation that if the wavelength of the x-rays is known, then the atomic spacing d can be determined by measuring the angle at which reflection occurs. Conversely, if d is known, then the wavelength of the x-rays can be measured. In the use of x-ray diffraction for crystal orientation, all three quantities λ, θ_B, and d are known and the problem is always to determine the dihedral angle between the plane surface of a quartz piezoid and a particular set of atomic planes. The equipment used in doing so is described in the following sections.

The value of d for any set $(hk.l)$ of atomic planes in quartz can be determined if the two lattice parameters a and c are known. In quartz the values are

$$a = 4.903 \text{ Å} \quad \text{at } 25^\circ\text{C}$$

and

$$c = 5.392$$

$$d_{(hkl)} = \frac{a}{\sqrt{\frac{4}{3}(h^2 + hk + k^2) + (al/c)^2}}$$

It is also possible to compute the Bragg angle for any set of planes from the relationship

$$\sin^2 \theta_B = \frac{\lambda^2}{4}\left(\frac{4}{3}\,\frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2}\right)$$

The Bragg angles depend slightly on the temperature of the crystal through the variation of d with temperature. Most measurements are made at temperatures near room temperature (25°C) and the variation of θ_B with temperature can usually be neglected in quartz orientation.

Table 11.2 shows the Bragg angles and the B-M indices for a few of the atomic planes commonly used in quartz orientation. It is assumed that Cu $K\alpha_1$ radiation is used and that the temperature is 25°C. The values are considered to be the best values available at the present time. Work is continuing to refine the values, but this is of little consequence in quartz crystal orientation since it is not the absolute value of θ_B which is required but, as stated before, the dihedral angle between the atomic planes and the surface of the quartz plate or piezoid.

Equation (105) requires that $n\lambda/2d \leqslant 1$. It is usually not convenient to use Bragg angles near 0 or 90° because in the first case the incident beam enters the detector and in the second the detector blocks the incident beam. It is usually desirable to use first-order reflections because the intensity is greater. If $0.3d < \lambda < 2d$, then $10° < \theta_B < 80°$, which is a convenient range in which to work. It is thus apparent that the wavelength must be comparable to the spacing. This requirement is nicely satisfied by the Cu $K\alpha_1$ line and for this reason the x-ray tubes used in the crystal industry usually have copper targets. We often specify the value of the Bragg angle without mentioning that the use of the Cu $K\alpha_1$ radiation is understood.

CARE IN THE USE OF X-RAYS

Although the intensity of the x radiation used in crystal orientation is low and the equipment is well shielded, it must never be forgotten that exposure to x-rays at any level should be avoided. Operators

Table 11.2. The Bragg Angles and B-M Indices of the Atomic Planes Used in Quartz Crystal Orientation.*

Designation	B-M Indices	Bragg Angle
Y or *m* face	(10.0)	10°26′
X-planes	(2$\bar{1}$.0)	18°18′
Z-planes	(00.3)	25°19′
Used with BT-cut	(20.3)	34°03′
R face (major rhomb)	($\bar{1}$0.1)	13°19′
r face (minor rhomb)	(10.1)	13°19′
Used with SC- and IT-cuts	(12.2)	33°53′

*It is assumed that Cu $K\alpha_1$ radiation is used.

should be required to keep their hands out of and away from the direct beam. Appropriate radiation monitoring devices (dosimeters) should be used by all personnel working with x-ray diffraction equipment. Periodic inspections should be made to ensure that all shields are in place and that no leakage of radiation is occurring. Finally, permanent records of the radiation received, even if it is zero, should be kept on file.

SINGLE-CRYSTAL X-RAY DIFFRACTION SYSTEM

The simplest type of x-ray diffraction equipment consists of an x-ray tube and power supply, a set of collimating slits, a goniometer and a suitable chuck for holding the crystal blank, a nickel filter, and a detector. The arrangement of the apparatus is shown in Fig. 11.3.

The collimating slits S_1 and S_2 are used to define a parallel beam of x-rays which passes through the axis of rotation O of the goniometer. The nickel filter, having a thickness of the order of 0.01 mm, absorbs the $K\beta$ radiation and passes the more intense $K\alpha$ radiation. The quartz plate or blank is held in place by a vacuum chuck system consisting of three sapphire beads so disposed that the reflecting surface of the blank lies in the goniometer axis. The orientation errors which result from failure of the incident beam to intersect the goniometer axis are discussed at the end of this chapter.

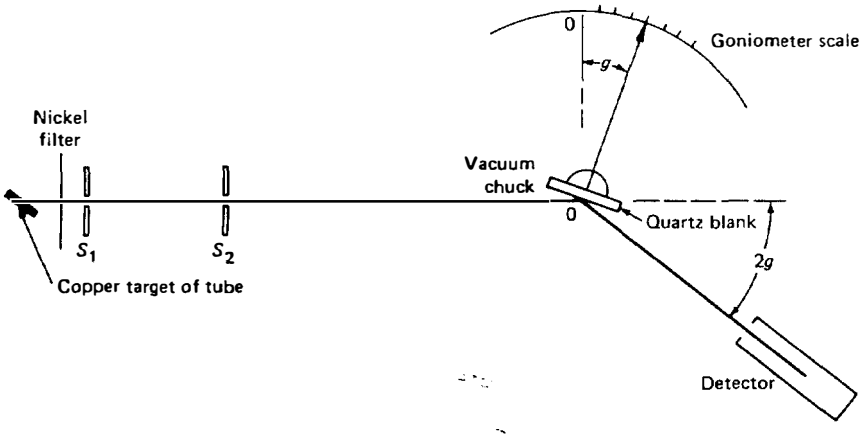

Fig. 11.3. The single-crystal diffraction system.

The goniometer should be capable of reading angles with an accuracy of 1′ of arc or better. It rotates the quartz blank about its center O, thereby varying the angle which the plane of the blank makes with the incident beam. When the angle between the atomic planes and the incident beam is equal to the Bragg angle θ_B, the beam is reflected and reaches the detector. Various types of detectors are used. High-intensity beams are usually detected by means of ionization chambers. Geiger (GM) counters with suitable integrating circuits are used with low-intensity beams. Solid-state detectors are also used.

The precision available with the apparatus just described is limited by the slit width and the natural line width of the $K\alpha$ radiation. It is usually not possible to resolve the $K\alpha_1$ and $K\alpha_2$ radiation with such apparatus. These wavelengths are reflected at angles differing typically by 2 to 5′ depending on θ_B. The minimum slit width is determined by intensity requirements. Because of these limitations orientation accuracy with the single crystal system is limited to about ± 5′ and in practical use even this accuracy is scarcely achievable.

DOUBLE-CRYSTAL X-RAY DIFFRACTION SYSTEM

It has become almost universal practice in the quartz crystal industry to use the double-crystal x-ray diffraction system which is illustrated in Fig. 11.4. The radiation from the x-ray tube is directed onto the surface of crystal A, which is called the collimating (or monochromator) crystal. Only that radiation which strikes crystal A at the correct Bragg angle is reflected, so that collimating slits and the nickel filter may be omitted. Crystal A is carefully prepared and permanently mounted to reflect the Cu $K\alpha_1$ radiation. The reflected radiation strikes the surface of crystal B, which is supported by the vacuum chuck in such a position that the axis O of the goniometer intersects the incident beam. The same reflecting planes should be used in both crystals. In this case Bragg reflection occurs at both crystals when the two sets of atomic planes are parallel to each other and to the goniometer axis.

Two conditions must be satisfied in order to take full advantage of the double-crystal system. First, the same reflecting planes must be used in both crystals and second, the atomic reflecting planes must

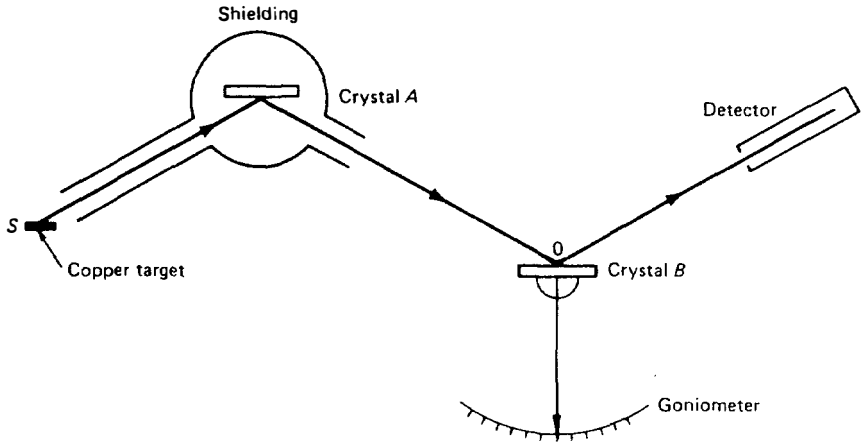

Fig. 11.4. Double-crystal x-ray diffraction system.

be parallel. In addition, it is desirable that the collimating crystal be nearer the x-ray tube. The positions of the fixed and moveable crystals may be interchanged without loss of accuracy but at some sacrifice of convenience and flexibility.

The advantages of the double-crystal system can be seen by considering Fig. 11.5. Here S is the focal spot on the target of the x-ray tube. The width of S is typically 2 to 3 mm. Each point on the focal spot emits x-rays of all wavelengths (see Fig. 11.1) in all directions. We consider the radiation in a band of wavelengths between λ_1 and λ_2 which may be the $K\alpha_1$ and $K\alpha_2$ or the $K\alpha$ and $K\beta$ radiations. Radiation of wavelength λ_1 is reflected from crystal A if and only if the Bragg relation is satisfied. Hence, radiation of wavelength λ_1 from every point on S is reflected at angle θ_{B_1} from *some* point on

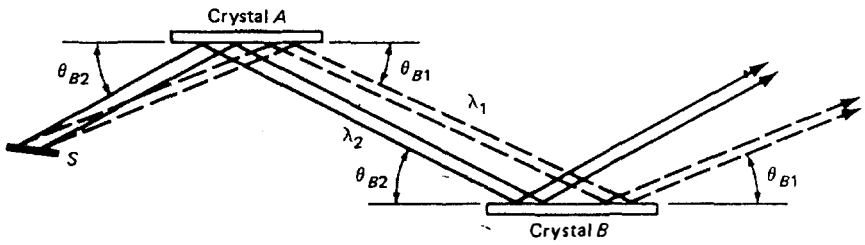

Fig. 11.5. Radiation of different wavelengths are simultaneously reflected at both crystals if they are in the parallel position.

crystal A. The same can be said for radiation of wavelength λ_2. The beams of wavelength λ_1 and λ_2, reflected from crystal A, are not parallel. Their angular separation can be calculated in the following way.

From the Bragg relation:

$$n\lambda = 2d \sin \theta_B$$

$$nd\lambda = 2d \cos \theta_B \; d\theta_B$$

Dividing the second equation by the first,

$$\frac{d\lambda}{\lambda} = \cot \theta_B \; d\theta_B$$

or

$$d\theta_B = \tan \theta_B \; \frac{d\lambda}{\lambda} \quad \text{radians} \tag{106}$$

If we let $d\lambda$ be the difference between the wavelengths of the $K\alpha_1$ and $K\alpha_2$ radiations and take $\theta_B = 13°19'$ corresponding to reflection from the (10.1) planes, we obtain

$$d\theta_B = \theta_{B_1} - \theta_{B_2} = 2.0'$$

After reflection from crystal A the two beams strike crystal B, which has the same diffraction constant (atomic spacing) as crystal A. If and only if the atomic planes of the two crystals are parallel, *both* beams are simultaneously reflected from crystal B. Thus the angular measurement compares the alignment of the atomic planes in the two crystals and the peak reading occurs when the two sets of planes are exactly parallel. The wavelength of the radiation need not be known.

If the lattice spacing of crystal B is not the same as that of crystal A or if the atomic planes of the two are not exactly parallel, then λ_1 may be reflected at crystal B but not at angle θ_{B_1}. Similarly λ_2 may be reflected but not at angle θ_{B_2}. Hence, in general, a "double peak" results, which is why the reflecting planes in the two crystals should be identical and parallel to the axis of the goniometer. Unless crystals A and B satisfy both these conditions, the advantages of the double-crystal system are not fully utilized.

Double-crystal reflection can be obtained with the crystals in the antiparallel position shown in Fig. 11.6, but in this position if

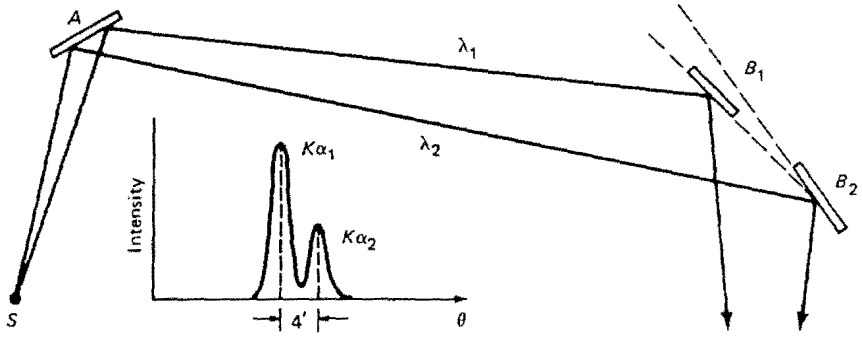

Fig. 11.6. The antiparallel position. Crystal A is fixed. B_1 is the position of crystal B to reflect λ_1 and B_2 is its position to reflect λ_2. The change in the angular position is given by $d\theta = 2 \tan \theta_B \, d\lambda/\lambda$. For Cu K_α radiation and the (10.1) planes $d\theta = 4.0'$. The insert shows the resulting double peak.

crystal B is set to reflect λ_1 it cannot reflect λ_2, and vice versa. For example, if crystals A and B employ the (10.1) planes and are set to reflect the $K\alpha_1$ radiation, one of the two crystals must be rotated by 4.0′ in order to reflect the $K\alpha_2$ radiation, thus resulting in the double peak mentioned above. Since the presence of the double peak may (and usually does) result in confusion, the antiparallel position should be avoided in designing a double-crystal diffraction system.

The intensity of the reflected radiation received by the detector is usually greater in the double-crystal system than in the single-crystal system despite the two reflections. This is because the radiation from the entire focal spot may be utilized, since no narrow collimating slits are required and also because a wider range of wavelengths is used. The width of the "rocking curve" (a plot of the intensity of the radiation received by the detector vs. the angular position of the crystal) depends not on the range of wavelengths, including the natural line width, but only on the broadening due to the crystal itself. In other words, the wavelength dispersion in the double-crystal system is zero, but the dispersion due to crystalline imperfections is not. In the single-crystal system both types of dispersion are present.

The most important cause of crystal dispersion is that of misoriented crystallites on the surface of the crystal. Any quartz surface which has been lapped or polished mechanically always has

misoriented crystallites on the surface. The degree of misorientation can be minimized by careful lapping and polishing, but etching with HF or NH_4F_2 deeply enough to remove the misoriented quartz is necessary to reduce the rocking curve to its limit of about 1′ of arc. The width cannot be reduced below this value for reasons which we cannot pursue here. When greater precision is required, it is necessary to find the center of the rocking curve by some means.

PREPARATION OF CRYSTAL STANDARDS AND COLLIMATING CRYSTALS

It is convenient and almost necessary in adjusting and aligning an x-ray system to have a set of "standard crystals." These are crystal blanks so cut that they have a major surface which is parallel to a given set of atomic planes. The surface of the blank should be polished and the angle adjusted until the blank can be rotated about an axis perpendicular to its reflecting surface without a change in the reflecting angle. This ensures that the atomic planes are parallel to the surface. Flatness should be checked with an optical flat. The blank should then be etched to remove all misoriented material as indicated by the width of the rocking curve. It will be noted that the intensity of the reflected beam decreases with etching.

Natural *r* or *R* faces are approximately parallel to the (10.1) planes and therefore provide a good start for preparing a (10.1) standard. But angle correction, polishing, and etching are still necessary to make a good standard.

Collimating crystals for use in double-crystal systems should be prepared in the same manner. Both standard and collimating crystals should be thick enough to prevent bending as they are mounted or used.

ANGLE MEASUREMENTS BY X-RAY DIFFRACTION

In the use of x-ray diffraction for crystal orientation, the object of all measurements is to determine the angle between a plane surface on the piezoid and a specified set of atomic planes. As a first example, suppose that we desire to make and check a *Y*-cut blank. The major surfaces of a *Y*-cut are normal to the *Y*-axis or parallel to the (10.0)

planes which have a Bragg angle of 10°26′. If the surface of the plate is exactly parallel to the (10.0) planes, then reflection of the $K\alpha_1$ radiation occurs when the incident beam makes an angle of 10°26′ with the surface of the plate and the plate can be rotated about an axis normal to its surface with no change in the goniometer reading. This case is shown in Fig. 11.7*a*.

In Fig. 11.7*b* we have the case in which the atomic planes make a dihedral angle δ with the surface of the plate; the line of intersection being parallel to the axis of the goniometer. Now the angle of incidence with the surface (not the atomic planes) is $\theta_B + \delta$ and the angle of reflection is $\theta_B - \delta$. In actual practice it is the angle δ which is required.

Now if the blank is rotated by 180° about the normal to its surface, the angle of incidence becomes $\theta_B - \delta$ and the angle of reflection $\theta_B + \delta$. The angle δ can be determined in either of two ways. We may use a standard blank in which $\delta = 0$, as shown in Fig. 11.7*a*, to determine θ_B and take the difference between this and the reading obtained from the blank, as shown in Fig. 11.7*b*. Alternatively we may take one reading, rotate the blank in its plane by 180°, and take a second reading. One-half the sum of the two readings is θ_B and one-half the difference is δ. However both readings must be made with the line of intersection of the atomic planes and the blank surface parallel to the goniometer axis.

The method of Fig. 11.7*b* is used to determine the *ZZ*′-angle of the AT-cut. (The *ZZ*′-angle is the angle between the plane of the blank and the *Z*-axis of the crystal.) If the AT-cut is properly made

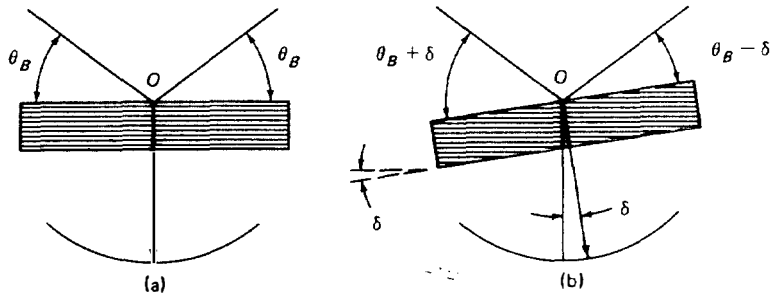

Fig. 11.7. The case in which the atomic planes are parallel to the surface of the blank is shown in (*a*). In (*b*) the atomic planes make a dihedral angle δ with the surface of the blank.

the angle δ between the surface of the blank and the (10.1) planes is about 3° (depending on the application) and the line of intersection of the planes is parallel to the X-axis. The quartz blank is placed on the chuck with the X-axis parallel to the axis of the goniometer. In the reflecting position the goniometer reading $g = \theta_B \pm \delta$, the sign depending on whether the X-axis points up or down. The ZZ'-angle is then either 38°13′ + δ or 38°13′ − δ. The correct position is, of course, 38°13′ − δ. Care must be taken to avoid the mistake of cutting the blank at 38°13′ + δ, because the resulting blank will have a large negative temperature coefficient. This mistake may not be observed with a single x-ray measurement.

ANGLE MEASUREMENTS WHEN THE AT NES DO NOT CONTAIN THE GONIOMETER AXIS

The first case which we examine is that in which the line of intersection of the atomic planes and the blank surface is perpendicular to the goniometer axis, as shown in Fig. 11.8. The plane of the surface of the blank is parallel to OO, the goniometer axis, but the atomic planes make an angle δ with it. The incident beam and the

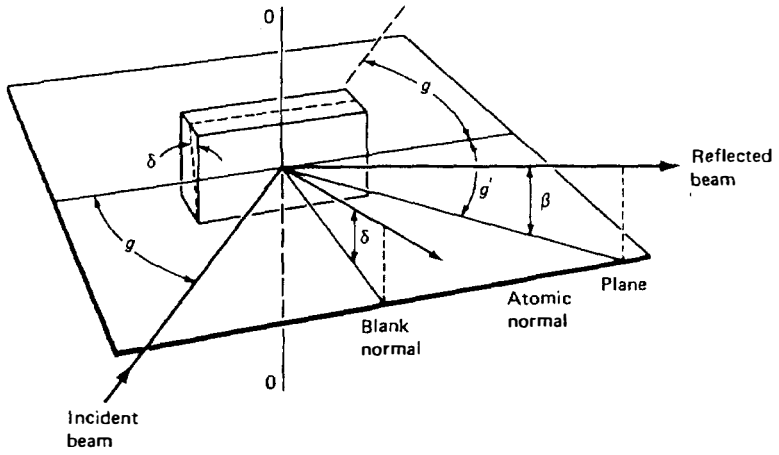

Fig. 11.8. The atomic planes make an angle δ with the blank surface which contains the goniometer axis 00. The line of intersection of the atomic planes and the blank surface lies in the plane of the instrument which is perpendicular to 00. (Adapted from R. A. Heising, *Quartz Crystals for Electrical Circuits*. New York: Van Nostrand, 1946, p. 112.)

normal to the blank lie in the plane of the instrument, but the normal to the atomic planes and the reflected beam do not do so.

The incident beam, the normal to the atomic planes, and the reflected beam lie in a plane which is called the *reflection plane.* In this plane the angle of incidence is θ_B and the detector setting is $2\theta_B$. However, the angles are not measured in this plane but in the plane of the instrument. Therefore, the goniometer reading g and the detector setting $g + g'$ are the projections of the angles θ_B and $2\theta_B$ on the plane of the instrument. The relationships between these quantities are[1]

$$\sin g = \frac{\sin \theta_B}{\cos \delta} \qquad 0 \leqslant \delta < 90° - \theta_B \tag{107}$$

and

$$\tan g' = \tan g \cos 2\delta \tag{108}$$

For example, if an AT-cut blank in which $\delta = 2°58'$ is placed on the goniometer chuck with the X-axis normal to OO (Fig. 11.8), reflection is obtained from the (10.1) planes for which $\theta_B = 13°19.0'$ at

$$g = 13°20'$$

and

$$g' = 13°16'$$

making the detector angle $g + g' = 26°36'$ instead of $26°38'$. Thus the "apparent Bragg angle" g is larger than the actual Bragg angle by about $1'$. Usually this difference is negligible. If, however, the angle δ were larger, say $10°$, then from Eq. (107) $g = 13°32'$, thereby requiring a correction of $13'$. From Eq. (108) the value of $g' = 12°45'$, thereby making the detector position $g + g'$ have the value of $26°17'$.

If δ is large the reflected beam may be directed above or below the detector. The angle β by which the reflected beam is directed above or below the goniometer plane is given by

$$\sin \beta = 2 \sin \delta \sin \theta_B = \sin 2\delta \sin g \tag{109}$$

In the last example where $\theta_B = 13°19'$ and $\delta = 10°$ we have $\beta = 4°35'$.

[1] The derivations of Eqs. (107) through (112) are given at the end of this chapter.

It is therefore apparent that the atomic planes used in checking the orientation of a given blank should make a small dihedral angle with the surface of the blank; otherwise corrections may be required for the errors introduced and relocation of the detector may be necessary.

THE EFFECT OF ROTATION IN THE PLANE OF THE BLANK

In measuring the ZZ' angle of the AT-cut blank it has been assumed that the X-axis lies in the plane of the blank and is parallel to the goniometer axis. Likewise, in measuring the XX' angle, the X-axis was assumed to be perpendicular to the goniometer axis. Errors are introduced if these conditions are not satisfied. We now investigate this source of error.

Let ψ be the angle of rotation of the blank about a normal to its surface. We assume that the line of intersection of the atomic planes and the blank surface is the X-axis and that $\psi = 0$ when the X-axis lies in the goniometer plane. Equation (110*a*) relates the angular position ψ with the goniometer reading g.

$$\cos^2 \theta_B = \sin^2 \delta \cos^2 \psi + (\cos g \cos \delta - \sin g \sin \delta \sin \psi)^2 \qquad (110a)$$

Equation (110*a*) can be solved only by approximation methods, which is rather tedious. Equation (110*b*) gives values of g to a very high degree of approximation for all reasonable values of δ and is easily soluble for g.

$$\sin (g + \delta \sin \psi) \doteq \frac{}{\cos (\delta \cos \psi)} \qquad (110b)$$

Both equations reduce to $g = \theta_B$ if $\delta = 0$ for all values of ψ; to $g = \theta_B - \delta$ if $\psi = 90°$ and to $g = \theta_B + \delta$ if $\psi = 270°$ and to Eq. (107) if $\psi = 0$.

The extreme values of g occur at the positions $\psi = 90°$ and $270°$, where $g = \theta_B \pm \delta$ thereby providing a method for determining the position $\psi = 0$ when the X-axis lies in the goniometer plane.
ever $g \neq \theta_B$ at $\psi = 0°$ or $180°$ but at angles slightly above 0
below $180°$. We have already seen that in the case of the AT-cut, if

$\psi = 0$, the difference between g and θ_B is about 1′. Figure 11.9 shows the manner in which g varies with ψ.

It is important to know how much error is introduced into the measurement of the ZZ' angle by errors in the angle ψ. As an example we take $\psi = 80°$, $\delta = 2°58'$, and $\theta_B = 13°19'$. Substituting these values in Eq. (110*b*) we find $g = 10°23.7'$. When $\psi = 90°$, $g = (\theta_B - \delta) = 10°21'$. Therefore an error of 2.7′ is introduced by a rotation of the blank by 10° about its normal. A similar calculation shows that a rotation of ± 5° introduces an error of only 0.7′.

CHECKING DOUBLY ROTATED BLANKS BY X-RAY DIFFRACTION

In the rotated Y-cut family which includes the AT- and BT-cuts as well as several others, the line of intersection of a suitable set of atomic planes and the surface of the blank is the X-axis. However, several cuts are known for which this is not the case; one example being the SC-cut (stress compensated) which is quite important because its frequency is substantially independent of stresses in the plane of the blank. We now show how x-ray diffraction may be used to determine the orientation of blanks such as the SC-cut.

It is convenient to specify the orientation of atomic planes and surfaces of blanks by the angles θ and ϕ in the coordinate system shown in Fig. 11.10. The angle θ is the angle between the Z-axis and the plane of the blank or the atomic plane. The angle ϕ is the angle between the X-axis and the line of intersection of the blank or atomic plane with the XY-plane of the coordinate system.

A blank which can be generated by a single rotation about one of the XYZ-crystallographic axes is called a *singly rotated* blank. The AT- and BT-cuts are examples of singly rotated blanks. If two rota-

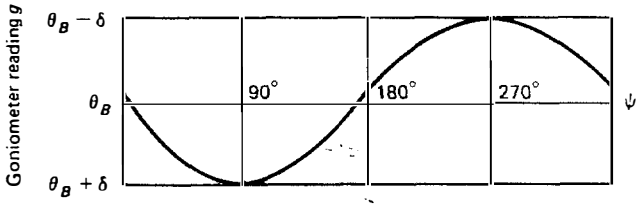

Fig. 11.9. Variation of the goniometer reading with the angle ψ for the AT-cut.

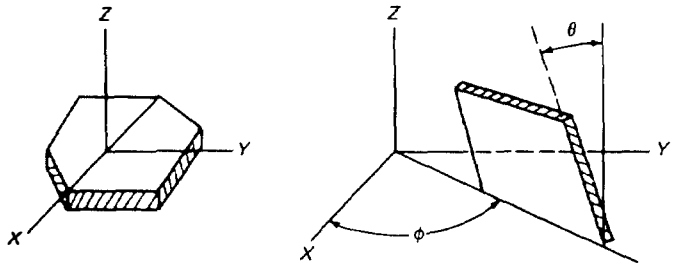

Fig. 11.10. Orientation of a double rotation plane in quartz.

tions are required the blank is said to be *doubly rotated.* Examples are the IT- and SC-cuts.

We have already seen that checking the value of θ for a singly rotated cut is relatively simple. It is only necessary to measure the angle between the surface of the blank and the atomic planes and then to add this angle to the value of θ for the atomic planes being used. Checking for a possible error in the XX' angle, which is really a ϕ angle, is a bit more complicated if the angle between the surface of the blank and the atomic planes is not very small. Such a blank is really a doubly rotated cut.

Table 11.3. Values of θ, ϕ, and θ_B for Some of the Planes Used in Orienting Quartz Piezoids.

Designation	θ	ϕ	Bragg angle θ_B
X-cut	0°	90°	
(11.0)	0°	90°	18°18′
Y-cut	0°	0°	
(10.0)	0°	0°	10°26′
AT-cut	35°15′*	0	
(10.1)	38°13′	0	13°19′
BT-cut	49°*	60°	
(20.3)	49°44′	60°	34°03′
IT-cut	34°20′*	19°06′	
(12.2)	30°46′	19°06′	33°53′
SC-cut	34°07′*	21°56′*	

*These angles are subject to small variations depending on the particular applications.

Checking the orientation of a doubly rotated cut is complicated if it happens that neither θ nor ϕ is the same for the blank and any set of atomic planes. Nevertheless, the orientation can be checked with arbitrary accuracy by a method to be described. Later we will use the SC-cut to illustrate the process.

We assume that the blank has been cut in such a way that one edge, which we will call the "reference edge," lies in the XY-plane. This presents no problem, since the XY-plane can be cut on the original crystal, checked by x-ray diffraction, and corrected if necessary. In fact, the manufacturers of cultured quartz supply "prelumbered" bars with accurately oriented XY- and YZ-surfaces. These surfaces can be painted and later identified on the blanks cut from the crystal.

We begin by defining two difference angles (see Fig. 11.13).

$$D_\theta = \theta_{\text{blank}} - \theta_{(hk.l)}$$

and

$$D_\phi = \phi_{\text{blank}} - \phi_{(hk.l)}$$

We assume that D_θ and D_ϕ are small, i.e., that a set of atomic planes exists near the required cut. Values of D_θ and D_ϕ as large as 10 or 15° are tolerable although smaller values are certainly desirable.

The blank is placed on the x-ray chuck with the reference edge vertical (parallel to the goniometer axis). The angle at which reflection is observed is read on the goniometer and designated g_θ. The blank is then placed on the chuck with the reference edge horizontal. The angle read is called g_ϕ.

Now if both D_θ and D_ϕ were zero, we should have $g_\theta = g_\phi = \theta_B$.

If either D_θ or D_ϕ were zero, the value of the other would be

$$D_\theta = g_\theta - \theta_B \qquad (D_\phi = 0)$$

$$D_\phi = g_\phi - \theta_B \qquad (D_\theta = 0)$$

If neither D_θ nor D_ϕ is zero or negligibly small, then we must write

$$\sin (g_\theta - D_\theta) = \frac{\sin \theta_B}{\cos D_\phi} \tag{111}$$

and

$$\sin (g_\phi - D_\phi) = \frac{\sin \theta_B}{\cos D_\theta} \tag{112}$$

The proofs of Eqs. (111) and (112) are given at the end of this chapter.

We can find the values of D_θ and D_ϕ satisfying these two equations by a process of iteration which converges very rapidly because the value of one of the quantities has only a second-order effect on the other.

We take for a zeroth approximation

$$_0D_\theta = g_\theta - \theta_B$$

and use this value of D_θ to calculate the first approximation to D_ϕ. Using Eq. (112),

$$\sin(g_\phi - {}_1D_\phi) = \frac{\sin\theta_B}{\cos {}_0D_\theta}$$

Then using the value of ${}_1D_\phi$ thus found, we substitute in Eq. (111) to find ${}_1D_\theta$. Continuing the process for two or three steps enables one to find the values of D_θ and D_ϕ. The process converges so rapidly that even for values of D_θ and D_ϕ as large as 10°, the results are accurate to 0.001° after three iterations.

The values of θ and ϕ for the blank are then given by

$$\theta_{\text{blank}} = \theta_{(hk.l)} + D_\theta \qquad \text{and} \qquad \phi_{\text{blank}} = \phi_{(hk.l)} + D_\phi \tag{113}$$

The procedure is a bit tedious even with a hand calculator. But with a programmable calculator or a computer it is only necessary to supply the values of g_θ and g_ϕ to obtain the values of the orientation angles θ and ϕ of the blank.

We will now illustrate the process by computing the values of θ and ϕ for an SC-cut blank. The example chosen is a rather extreme case for purposes of illustration; ordinarily the initial cut would be made closer to the required orientation. The (12.2) planes are used. Note that the collimating crystal should also use the same planes to avoid a double peak.

For purposes of illustration we assume goniometer readings of

$$g_\theta = 47.000° \qquad \text{and} \qquad g_\phi = 29.000°$$

(If the SC-cut were intended to have angles $\theta = 34°07'$ and $\phi = 21°56'$, the values of g_θ and g_ϕ, respectively, should be $37°16'$ and

36°48′. Thus in the hypothetical example the blank is cut far from the correct orientation.)

The Bragg angle θ_B for the (12.2) planes is 33.8833°. In the zeroth approximation

$$ {}_0D_\theta = g_\theta - \theta_B = 13.1167^\circ \qquad \text{and} \qquad {}_0D_\phi = g_\phi - \theta_B = -4.8833^\circ $$

We may now use either of these values to calculate a first approximation to the other. Thus using Eq. (111),

$$ \sin(g_\theta - {}_1D_\theta) = \frac{\sin\theta_B}{\cos {}_0D_\phi} $$

we have $$ {}_1D_\theta = 12.9764^\circ $$

This value may now be used with Eq. (112) to compute ${}_1D_\phi$; thus

$$ \sin(g_\phi - {}_1D_\phi) = \frac{\sin\theta_B}{\cos {}_1D_\theta} $$

from which $$ {}_1D_\phi = -5.8977^\circ . $$

Continuing in this way we obtain

$$ {}_2D_\theta = 12.9117^\circ \qquad \text{and} \qquad {}_2D_\phi = -5.8874^\circ $$

and $$ {}_3D_\theta = 12.9124^\circ \qquad \text{and} \qquad {}_3D_\phi = -5.8875^\circ $$

Further iterations produce no changes greater than 0.0001°, so we take for the blank

$$ D_\theta = 12^\circ 55' \qquad \text{and} \qquad D_\phi = -5^\circ 53' $$

and since $\theta_{\text{blank}} = \theta_{(hk.l)} + D_\theta$ and $\phi_{\text{blank}} = \phi_{(hk.l)} + D_\phi$

we have $$ \theta_{\text{blank}} = 30^\circ 46' + 12^\circ 55' = 43^\circ 01' $$

and $$ \phi_{\text{blank}} = 19^\circ 06' + (-5^\circ 33') = 13^\circ 33' $$

Thus the value of θ for this hypothetical blank is about 9° too large and the value of ϕ is about 8° too small. Even in this case adequate convergence is obtained in three iterations. If D_θ and D_ϕ are larger, more iterations are required but there is little reason for blanks being cut this far from a set of atomic planes.

ERRORS DUE TO MISALIGNMENT OF THE INCIDENT BEAM

In aligning an x-ray system it is extremely important that the incident beam intersect the goniometer axis. We now investigate the errors resulting from failure to do so. We assume, for simplicity, that the atomic planes in the blank are parallel to the surface of the blank. In a perfectly aligned system the incident beam strikes the crystal at point O (Fig. 11.11), which is the center of the goniometer circle G of radius R. The goniometer reading is θ_B.

Now suppose the goniometer axis and the crystal plate are shifted a distance a in a direction perpendicular to the plate. This moves O to O' and G to G'. The beam now strikes the crystal at point P. The angles of incidence and reflection are still θ_B but the angle measured by the goniometer is now angle g instead of angle θ_B. By considering the geometry of the situation we see that

$$\sin g = \frac{SA}{R} \qquad \text{and} \qquad \tan \theta_B = \frac{SA}{AP}$$

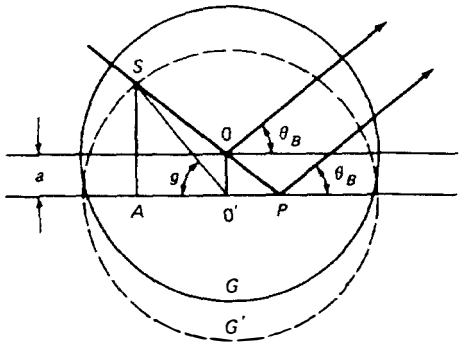

Fig. 11.11. Result of x-ray beam not intersecting the goniometer axis.

Therefore

$$\sin g = \frac{AP \tan \theta_B}{R}$$

But

$$AP = AO' + O'P = R \cos g + a \cot \theta_B$$

from which

$$\boxed{\tan \theta_B = \tan g - \frac{a}{R} \cos g}$$

The difference between θ_B and g may be quite significant. For example, suppose the radius of the goniometer circle to be 50 cm and that distance a is 0.1 cm. If the goniometer reading is 15.000°, the true value of θ_B is 14.889°, which is a difference of nearly 7′. Thus a displacement of only 1 mm in the position of the axis of the goniometer, in a typical case, introduces an error of almost 7′ in the angle measurement. This is a common error in making an x-ray diffraction measurement and doubtless accounts for many of the discrepancies between measurements made on different machines.

No error results from failure of the reflecting surface of the crystal plate to contain the goniometer axis O so long as the incident beam passes through O (or would do so if the plate were removed). Thus measurements may be made from either side of a thick plate with parallel surfaces.

DERIVATIONS OF EQUATIONS (107) to (110)

In Fig. 11.8 the incident beam lies in the plane of the goniometer as does the blank normal. The atomic planes make an angle δ with the goniometer axis. If $\delta = 0$, the goniometer reading g is equal to the Bragg angle θ_B and the incident beam, the reflected beam, and the normal to the atomic planes all lie in the goniometer plane.

If $\delta \neq 0$, then the normal to the atomic planes and the reflected beam no longer lie in the goniometer plane although, of course, the incident beam does do so. The plane containing the incident beam, the reflected beam, and the normal to the atomic planes is called

the *reflection plane.* The incident beam lies along the intersection of the reflection plane and the goniometer plane. In the reflection plane the angles of incidence and reflection are the Bragg angle θ_B. The goniometer measures angle g, which is the projection of the angle of incidence on the goniometer plane.

We define a coordinate system XYZ in which the goniometer plane is the XY plane and the Z axis is the goniometer axis. (See Fig. 11.12.) The atomic planes intersect the XY plane along the X axis and make an angle δ with the Z axis.

When $\delta = 0$ we define a vector of unit length $\mathbf{V}_1$ along the incident beam and a unit vector $\mathbf{N}_1$ along the normal to the atomic planes, both of course lying in the XY, or goniometer, plane. The components of $\mathbf{V}_1$ are (cos θ_B, sin θ_B, 0), and the components of $\mathbf{N}_1$ are (0, 1, 0). Therefore the cross product $\mathbf{V}_1 \mathbf{X} \mathbf{N}_1$ is a vector having components (0, 0, cos θ_B). The magnitude of this vector, which is cos θ_B, is the area of the parallelogram formed on $\mathbf{V}_1$ and $\mathbf{N}_1$. (See Fig. 11.14.)

We now assume that $\delta \neq 0$ and define unit vectors $\mathbf{V}_2$ and $\mathbf{N}_2$ both of which lie in the reflection plane. Vector $\mathbf{V}_2$, which lies along the incident beam, has components (cos g, sin g, 0). Vector $\mathbf{N}_2$, which

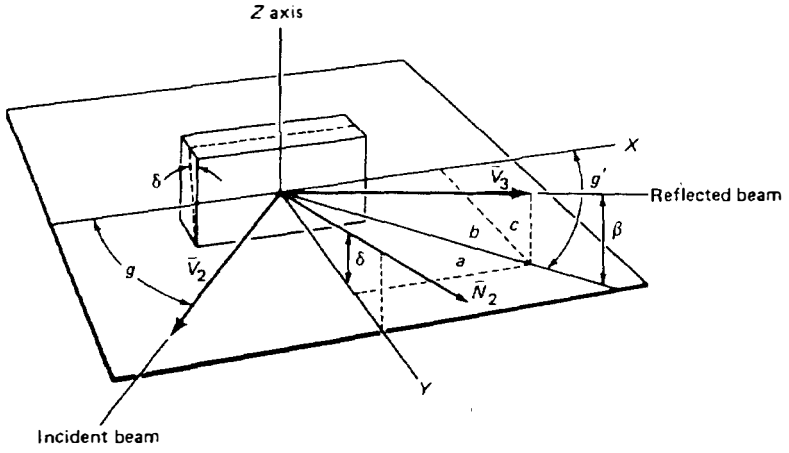

Fig. 11.12. The coordinate axes X and Y lie in the goniometer plane and the axis Z, which contains the goniometer axis, is perpendicular to it. The unit vectors $\mathbf{V}_2$, $\mathbf{N}_2$, and $\mathbf{V}_3$ lie in the reflection plane.

lies along the normal to the atomic planes, has components (0, cos δ, sin δ). The vector product[2] $\mathbf{V}_2 \times \mathbf{N}_2$ is a vector having components (sin g sin δ, – cos g sin δ, cos g cos δ). The magnitude of this vector is equal to the area of the parallelogram formed on $\mathbf{V}_2$ and $\mathbf{N}_2$ (in the reflecting plane), which must be equal to the area of the parallelogram formed on $\mathbf{V}_1$ and $\mathbf{N}_1$. This follows from the fact that the angles between both pairs of vectors is θ_B and all of the vectors are unit vectors. Therefore

$$\cos^2 \theta_B = \sin^2 g \sin^2 \delta + \cos^2 g \sin^2 \delta + \cos^2 g \cos^2 \delta$$

from which

$$\sin g = \frac{\sin \theta_B}{\cos \delta} \tag{107}$$

We now define a unit vector $\mathbf{V}_3$ lying along the reflected beam and having components (a, b, c). The vector product $\mathbf{N}_2 \times \mathbf{V}_3$ is a vector having components (c cos δ – b sin δ, a sin δ, $-a$ cos δ). This vector is the area of the parallelogram formed on $\mathbf{N}_2$ and $\mathbf{V}_3$. It is equal to the vector representing the area of the parallelogram formed on $\mathbf{V}_2$ and $\mathbf{N}_2$. This is true because both areas are equal in magnitude and are coplanar. We thus have the three equations

$$\begin{aligned} c \cos \delta - b \sin \delta &= \sin g \sin \delta \\ a \sin \delta &= -\cos g \sin \delta \\ -a \cos \delta &= \cos g \cos \delta \end{aligned}$$

The last two equations define the value of a, which is

$$a = -\cos g$$

From the first equation $b = c \cot \delta - \sin g$.
We also have, since $\mathbf{V}_3$ is a unit vector,

$$a^2 + b^2 + c^2 = 1$$

[2] See page 206 for the definition of the vector (or cross) product.

Eliminating a and b from the last three equations we obtain

$$c = 2 \sin \delta \cos \delta \sin g$$

and using $$\sin g = \frac{\sin \theta_B}{\cos \delta}$$

we have $$c = 2 \sin \delta \sin \theta_B$$

The angle g' which determines the detector setting is defined by

$$\tan g' = \frac{b}{a} = \frac{c \cot \delta - \sin g}{-\cos g}$$

which simplifies to

$$\tan g' = \tan g \cos 2\delta \tag{108}$$

The angle β is the angle between the reflected beam and the goniometer plane. Therefore $c = \sin \beta$ and thus

$$\sin \beta = 2 \sin \delta \sin \theta_B = \sin 2\delta \sin g \tag{109}$$

We now consider the effect of rotating the blank by an angle ψ about a normal to the blank. It is assumed that the line of intersection of the atomic planes and the surface of the blank lies in the plane of the goniometer when $\psi = 0$. (In the AT-cut the line of intersection is the crystallographic X-axis.)

We define a unit vector $\mathbf{V}_4$ which lies along the incident beam having components ($\cos g$, $\sin g$, 0). Vector $\mathbf{N}_4$ is a unit vector normal to the atomic planes in the blank having components ($\sin \delta \cos \psi$, $\cos \delta$, $\sin \delta \sin \psi$). The vector product $\mathbf{N}_4 \times \mathbf{V}_4$ is a vector having components

$$(\sin g \sin \delta \cos \psi, \cos g \sin \delta \sin \psi, \sin g \sin \delta \sin \psi - \cos g \cos \delta)$$

Just as before, the magnitude of this vector must be equal to $\cos \theta_B$ and therefore

$$\cos^2 \theta_B = \sin^2 \delta \cos^2 \psi + (\cos g \cos \delta - \sin g \sin \delta \sin \psi)^2 \tag{110a}$$

Equation (110*a*) is the exact relationship between the goniometer angle g and the variables θ_B, δ, and ψ. Unfortunately it cannot be solved in closed form for the value of g and must be solved numerically by successive approximations. Fortunately there exists an approximate equation which is easily solved for g and which gives excellent agreement with the exact equation for all reasonable values of δ. The equation is

$$\sin(g + \delta \sin \psi) \doteq \frac{\sin \theta_B}{\cos(\delta \cos \psi)} \qquad (110b)$$

For instance, if we take $\delta = 3.0000°$, $\theta_B = 13.0000°$, and $\psi = 45°$, Eq. (110*b*) gives $g = 10.8878°$ whereas the correct value from Eq. (110*a*) is $g = 10.8868°$ – a difference of about 3″ of arc. The agreement is better for values of ψ near 0°, 90°, 180°, etc., and worse for larger values of δ. The agreement is exact at 90°, 180°, 270°, etc. If we take $\delta = 10°$, $\theta_B = 13°$, and $\psi = 45°$, the value of g from Eq. (110*b*) is 5.994° whereas the correct value from Eq. (110*a*) is 6.0303°, a difference of about 2′ of arc. This is a rather extreme case and it should seldom be necessary to have a difference this large.

DERIVATION OF EQUATIONS (111) AND (112)

Doubly rotated plates present a special case of x-ray orientation and measurement. We now define the equations relating the two goniometer readings with the orientation angles θ and ϕ. Figure 11.13

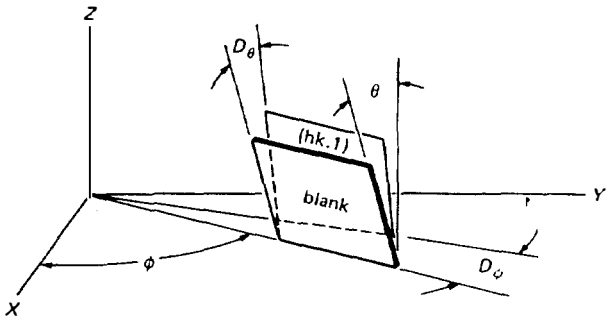

Fig. 11.13. Position of the blank relative to the (*hk*.1) planes. The axes are the crystallographic axes.

shows the positions of the blank and the $(hk.l)$ planes used to orient the blank relative to the crystallographic XYZ-axes.

We let $D_\theta = \theta_{\text{blank}} - \theta_{(hk.l)}$ and $D_\phi = \phi_{\text{blank}} - \phi_{(hk.l)}$

We first calculate the value of g_θ which is the goniometer reading when the blank is in the position for measuring the angle θ (see Fig. 11.12). We assume that the normal to the blank lies in the goniometer plane and is parallel to the Y axis. The $(hk.l)$ planes make angles D_θ and D_ϕ with the surface of the blank, as shown in Fig. 11.13.

We now define a unit vector $\mathbf{N}_5$ perpendicular to the $(hk.l)$ planes. This vector has components (Fig. 11.12)

$$(-\sin D_\theta \cos D_\phi, \cos D_\theta \cos D_\phi, \sin D_\phi)$$

As before, the unit vector $\mathbf{V}_5$ along the incident beam has components

$$(\cos g_\theta, \sin g_\theta, 0)$$

The cross product $(\mathbf{V}_5 \times \mathbf{N}_5)$ is a vector having components

$$(\sin g_\theta \sin D_\phi, -\cos g_\theta \sin D_\phi, \cos g_\theta \cos D_\theta \cos D_\phi + \sin g_\theta \sin D_\theta \cos D_\phi)$$

The magnitude of the vector $(\mathbf{V}_5 \times \mathbf{N}_5)$ is the area of the parallelogram formed on $\mathbf{V}_5$ and $\mathbf{N}_5$ in the reflection plane. This parallelogram has the same area as that formed on $\mathbf{V}_1$ and $\mathbf{N}_1$ in the goniometer plane since the angle between both pairs of vectors is the complement of θ_B. The magnitude of the vector $(\mathbf{V}_5 \times \mathbf{N}_5)$ is $\sin(90^\circ - \theta_B) = \cos\theta_B$ and therefore

$$\cos^2\theta_B = \sin^2 g_\theta \sin^2 D_\phi + \cos^2 g_\theta \sin^2 D_\phi + (\cos g_\theta \cos D_\theta \cos D_\phi + \sin g_\theta \sin D_\theta \cos D_\phi)^2$$

which reduces readily to

$$\sin(g_\theta - D_\theta) = \frac{\sin\theta_B}{\cos D_\phi} \qquad (111)$$

Placing the blank in the position to measure the crystallographic angle ϕ merely interchanges the two angles D_θ and D_ϕ so that by exactly the same reasoning it follows that

$$\sin (g_\phi - D_\phi) = \frac{\sin \theta_B}{\cos D_\theta} \tag{112}$$

In practice the values of g_θ and g_ϕ are measured by x-ray diffraction and the value of θ_B is known. Hence Eqs. (111) and (112) uniquely determine the values of D_θ and D_ϕ the values of which can be calculated with arbitrary accuracy by an iteration method. The orientation angles θ and ϕ for the blank are then found by adding D_θ and D_ϕ to the values of θ and ϕ for the atomic planes.

****

A vector $\mathbf{V}$ can be expressed in terms of its scalar components a, b, and c as

$$\mathbf{V} = a\mathbf{i} + b\mathbf{j} + c\mathbf{k}$$

where $\mathbf{i}$, $\mathbf{j}$, and $\mathbf{k}$ are unit vectors along X, Y, and Z, respectively.

The scalar product of two vectors $\mathbf{V}_1 = a_1\mathbf{i} + b_1\mathbf{j} + c_1\mathbf{k}$ and $\mathbf{V}_2 = a_2\mathbf{i} + b_2\mathbf{j} + c_2\mathbf{k}$ is $\mathbf{V}_1 \cdot \mathbf{V}_2 = a_1a_2 + b_1b_2 + c_1c_2 = V_1V_2\cos\theta$, where V_1 and V_2 are the magnitudes of the vectors and θ is the angle between them.

The vector product of the two vectors $\mathbf{V}_1$ and $\mathbf{V}_2$ is

$$\mathbf{V}_1 \mathbf{X} \mathbf{V}_2 = \begin{vmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \\ a_1 & b_1 & c_1 \\ a_2 & b_2 & c_2 \end{vmatrix} = (b_1c_2 - b_2c_1)\mathbf{i} + (a_2c_1 - a_1c_2)\mathbf{j} + (a_1b_2 - a_2b_1)\mathbf{k}$$

$$= V_1 V_2 \sin\theta \, \mathbf{n}$$

where $\mathbf{n}$ is a unit vector perpendicular to $\mathbf{V}_1$ and $\mathbf{V}_2$.

The vector product $\mathbf{V}_1 \mathbf{X} \mathbf{V}_2$ is obviously the area of the parallelogram formed on $\mathbf{V}_1$ and $\mathbf{V}_2$ (see Fig. 11.14).

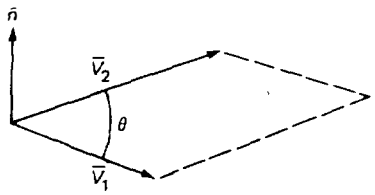

Fig. 11.14. The vector product of two vectors is the area of the parallelogram formed on the two vectors.